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THE  
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*A Journal of Practical Chemistry*

IN ALL ITS APPLICATIONS TO

**PHARMACY, ARTS, AND MANUFACTURES.**

EDITED BY

**SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.**

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# THE CHEMICAL NEWS.

VOLUME CXI.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., Pres.R.S., &c.

No. 2875.—JANUARY 1, 1915.

## GERMAN METHODS IN COMMERCE.\*

By Sir WILLIAM RAMSAY, F.R.S., D.C.L., LL.D., &c.

It has not been generally known that in commerce, as in war, the methods employed by Germany have been completely organised for many years. Instead of looking on commerce as an arrangement for mutual benefit, the German nation has regarded it as a war. And, just as in the present war, all methods of attack are regarded by the military advisers of Germany as legitimate, so we are slowly awaking to the knowledge that German commercial and industrial methods have for years been aggressive. The war in which we are now engaged is, indeed, a war for the liberation of nations from commercial and industrial brutality, as well as for their deliverance from an attempted enslavement to German "Kultur," as exemplified by the practices of their army.

At the annual meeting of the Society of Chemical Industry in 1903, I pointed out that the German military organisation had its counterpart in their commercial organisation; that there exists an Imperial Council whose proceedings are kept quiet, but which takes into consideration all obtainable statistics, and as far as possible legislates, or endeavours to legislate, on the basis of these statistics. Where fiscal duties are found to be required, they are imposed on them, not where there is an advantage in doing so, but where they give it; for the railways are the property of the State. I then said: "Is it to be expected that any country can fight such a combination as that without adopting, at all events, something of their methods, or without studying their methods, and without combining together, if not to imitate them, at least to thwart them? There is a military campaign against us, and we must defend ourselves."

The competition in the colour trade, for instance, has almost prohibited the manufacture of dyes in England. In Germany the management is in the hands of well-trained men, who, aided by an efficient staff of engineers and chemists, are continually engaged on the problems of utilising any discovery made in their own laboratories or elsewhere, and making it commercial, whether by securing cheap raw material, cheapening the process of manufacture, or creating a public demand for the object to be manufactured. Agencies are maintained all over the world whereby the article is introduced to the notice of foreign purchasers; and an extensive credit system is encouraged. All this is legitimate; but the maintenance of a trained legal staff, not merely to advise as to the validity of patents, but to advise whether the infringement of

another's patent is likely to be successful, and whether it may not be possible, by infringing a patent, so to saddle an opponent with legal expenses as to break his competition, is not easily defensible. Fair competition between individuals lies at the bottom of all trade; unfair competition, backed by all the resources of the State, is what we have had to face with Germany.

We have recently had brought to our notice German methods applied to the shipping industry, and the Australians have been pointing out that the control of the "base metal market" is almost entirely in German hands.

It is necessary to go further; just as the German State has shown itself to be no respecter of treaties, just as the leaders of the German Army have revealed themselves as breakers of every humane law, treacherous and deceitful, so long as they think they can gain their ends, so it is foolish not to be warned that the German nation as a whole is completely unworthy of trust; that commercial agreements are regarded by members of that nation as binding only so long as some advantage is to be gained by keeping to them; and that dishonesty is excusable if only it appears to lead to German prosperity. For there is a sort of debased patriotism in the average German mind—"Deutschland, Deutschland über alles, über alles in der Welt" and the notion that the supremacy of "Deutschland"

We were shocked at the beginning of the war by the disregard towards treaties displayed by our opponents; we were amazed at the treatment of Belgian non-combatants; and we are slowly realising that every trick, from firing on the Red Cross to the false display of the white flag of surrender, is made use of by the enemy, and not, as it is observed, by individual groups of our opponents, but by command from high quarters. We are slowly and incredulously awakening to the knowledge that German commercial tricks are on a par with their tricks in war; that the whole nation is infected by the microbes of dishonesty and dishonesty.

Of course there are honest men among our opponents; from time to time we read of kind acts to our wounded; and from a lifelong experience of Germany and the Germans I have no hesitation in stating there are Germans as kindly, as honest, and as upright as there are among ourselves, the French, the Americans, and among the inhabitants of all other nations. That is not the point. What we have to face is a nation organised for a policy of dishonesty, and a nation which, as a nation, approves of that policy. Moreover, this nation believes that the policy of dishonesty is likely to be a successful one, and it has the will, and believed itself to have the power, to enforce this policy on the whole world. Conscientious Germans

\* Read at the Institute of Industry and Commerce.

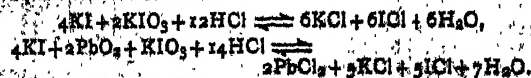
have been impressed more by the end than by the means adopted to gain that end: the prosperity of their "Vaterland."

I conceive that the main purpose of the Institute of Industry and Commerce is to take counsel and evolve some means for combating this attack. Just as it is clear that peace can never be declared until the chance of another Teutonic outburst is made impossible by the total disbandment of the German Army, so it must be evident that the commercial system of Germany cannot be allowed to continue. It is probable that it is better to make a beginning by an alliance of Science, Industry, and Commerce, such as the Institute contemplates; but it will be necessary, if the future German State is allowed to retain the power of waging an industrial war, to combat it by the action of the organised British nation, that is, by the State. Once that conquest is achieved, however, we should do well to remember that commerce should be co-operative and not competitive; that it is to our interest not only that we ourselves should prosper, but that others should also prosper; that, indeed, our own prosperity is bound up in the prosperity of our fellow-creatures.

#### DETERMINATION OF PEROXIDE IN COMMERCIAL LEAD OXIDE.

By L. S. DEAN.

TITRATION with potassium iodate has been suggested as a possible alternative for the Bunsen method by L. W. Andrews (*Journ. Am. Chem. Soc.*, 1903, xxiii., 792). This method has been found useful, especially for the determination of small percentages of peroxide, and in the presence of organic matter. The method consists in decomposing the peroxide by hydrochloric acid in the presence of potassium iodide, using chloroform or carbon tetrachloride as an indicator, and titrating back the excess of potassium iodide with potassium iodate. The iodate may be made up accurately by weighing out the pure salt, and the standard iodide is titrated against the iodate. The equations involved are:—



Hence,  $2PbO_2 = KIO_3$ .

A comparison of the results obtainable with this method and those obtainable with the Bunsen method is given below:—

Iodate method (per cent) ..	31.95	32.00	5.10	5.14	10.50
Bunsen method (per cent) ..	32.09	32.05	5.22	5.20	10.56

As shown above the method is as accurate as the Bunsen method, and presents many advantages, viz.:—

1. It requires no special apparatus.
2. It can be used in the presence of organic matter.
3. It is not necessary to dissolve all the oxide taken, since the indicator is not interfered with by solid material; this is of the greatest advantage in analysing litharge as large samples may be taken.

Laboratory of the Missouri School of Mines.

#### THE FRUIT OF *CLINTONIA BOREALIS*.

By HORACE A. SLIPPY.

THE fruit was gathered at Sylvan Beach, New York, August 1—4, 1913. It seemed fully ripe, as many of the berries had dropped from the stem. From one to seven berries grew upon each stalk. They were of oval shape, deep indigo blue in colour, and the average weight of each when dried was 0.0858 gm. The fresh fruit has a very bitter taste. It shrinks in drying to about one-fourth

of its original size and weight. Each berry contains from 15 to 20 small hard seeds.

The plant is called the *Clintonia*, after Governor De Witt Clinton, who built the Erie Canal and made several other improvements in New York State during his term of office.

#### The Ash.

Six different portions of the berries, using about 3 grms. each time, were ashed in a platinum evaporating dish. From the first portion silica, iron, alumina, calcium, and magnesia were determined; from the second sodium and potassium, by a modification of the J. Lawrence Smith method; from the third the sulphates; from the fourth the phosphates; and manganese from the fifth. When burned the odour at first reminded one of scorched pumpkin, and finally of burning corn. The results of the analysis were as follows:—

	Per cent of ash.
SiO <sub>2</sub> .. .. .	0.81
Al <sub>2</sub> O <sub>3</sub> .. .. .	2.29
Fe <sub>2</sub> O <sub>3</sub> .. .. .	2.82
CaO .. .. .	2.12
MgO .. .. .	7.56
K <sub>2</sub> O .. .. .	19.26
Na <sub>2</sub> O .. .. .	17.66
SO <sub>3</sub> .. .. .	5.85
P <sub>2</sub> O <sub>5</sub> .. .. .	25.73
MnO .. .. .	0.26
Cr .. .. .	—
Cl .. .. .	7.18
Total .. .. .	98.66

There was a small quantity of CO<sub>2</sub> which was not determined. The ash was 4.87 per cent of the dried fruit.

#### Proteins.

We were not able to detect the presence of albumen by the ordinary tests. When the berries were heated in a dry test-tube notable quantities of oil condensed on the sides of the tube. When heated in a dry tube with soda-lime the fumes given off reacted alkaline to litmus, and had a slight odour of ammonia. The nitrogen was determined by the Kjeldahl-Gunning method and found to be 1.05 per cent of the dried fruit.

#### The Sugars.

We placed 400 grms. of the dried fruit in a litre flask connected with an inverted condenser. It was treated with 95 per cent alcohol until a test with Fehling's solution showed only a trace of sugar. The alcoholic extract left a dark thick syrup when distilled. After standing some time the odour of the extract resembled that of old cider, showing that alcoholic fermentation had taken place. The last traces of sugar were extracted with water instead of alcohol. The water made them soft and mushy, whereas they were hardened by the alcohol. The water extraction was of a dark colour, and the work was continued until the sugar was all removed.

The two sugar solutions were treated with Fehling's solution of standard strength. We found 4.15 per cent of sugar in the water solution and 9.05 per cent in the alcoholic extract, a total of 13.20 per cent of sugar in the dried fruit. The water extract contained a gum-like substance which alcohol would precipitate. We obtained 38 grms. of this material. The osazone, obtained by the use of phenylhydrazine and sodium acetate, indicated the presence of glucose and fructose. Before making the test the sugar solution was purified by the use of bone-black.

#### Acids.

The acid tests were made from the sugar extract. Citric and tartaric acids were present in small amounts, as well as acetic resulting from the fermentation of the sugar.

### The Oils.

The residue from the sugar extraction when dried weighed 241 grms., and this was used for the extraction of the oils. It was ground very fine, placed in a litre flask fitted with an inverted condenser, and treated with ether. The process was continued for about eighteen weeks without being able to make the extraction complete. At first the oil was of a beautiful deep green colour, due to the presence of chlorophyll. It was purified by treating a solution in ether with bone-black, when it appeared as a beautiful clear light yellow oil, like sweet oil, with a sweetish taste. Its specific gravity at 15.5° was 0.897. This is low for a vegetable oil, but not far from the specific gravity of sperm oil and bottlenose oil. We then saponified 3.511 grms. of the oil by the Kottlander method, which gave as the saponification equivalent somewhat less than that of sperm oil and bottlenose oil. It was very difficult to saponify, which was effected only after long continued heating.

We regret that, owing to lack of time, we were not able to repeat this experiment. Although we did not succeed in extracting all the oil, we obtained 16.89 grms., or 4.22 per cent of the dried fruit.

I desire to express my thanks to Dr. N. Knight for his advice and assistance in this work.

Cornell College, November 6, 1914.

### ON IRON CASTING.

By SERGIUS KERN, M.E., Petrograd.

For several years I have read with great interest many papers in English technical literature concerning the use of steel in the form of sheatings from plates, angles, &c., or runners from steel castings, as an addition to the cupola pig-iron charge, in order to obtain strong close iron castings with high tensile and fracture tests.

After several years of practical experience I found that the above method is the most reliable, as compared with the use of a certain percentage of white irons to the cupola charge, for obtaining castings to stand hydraulic or steam pressure.

I desire to give an example of my *modus operandi*. At present I have pig-irons of the following percentage composition:

	Per cent.	Per cent.
Combined carbon	0.80	1.00
Manganese	0.50	1.50
Silicon (average)	2.70	0.85
Phosphorus	0.10	0.05
Sulphur	0.05	0.05

I melt in a crucible a test charge to contain about 2.15 of silicon, 3.50 of total carbon, 0.70 combined carbon, and 0.80 manganese (per cent), with steel shearings. In my instance I took for the crucible charge:—

	Per cent.
South Russia pig-iron	70
Ural pig-iron	30
Steel, on 100 per cent	100

The cast specimens gave 12.50 to 12.00 tons per square inch tensile strength, and 1.6 to 1.7 tons for fracture. The rounds for the first tests were 2 inches long and three-quarter inch diameter, and for the second 12 x 1 x 1 inches.

Being satisfied with such results, I make charges for our cupola consisting of 70 per cent of South Russia pig-iron, 30 per cent of Ural pig-iron, and 15 to 14.5 per cent of steel runners.

Obtained.—11.50 to 12.00 tons tensile strength and 1.5 to 1.5 tons for fracture tests. The castings obtained were close-grained and give good hydraulic tests.

### BRITAIN AND GERMANY IN RELATION TO THE CHEMICAL TRADE.\*

By WILLIAM REGINALD ORMANDY, D.Sc., F.C.S.

The subject which we have to discuss to-night is not by any means a new one. The fact that Germany has slowly but surely been gaining control of the greater part of the chemical industries of the world has been brought home to this country times innumerable during the last forty years. It is true that this control has not extended to the manufacture of what are known as heavy chemicals, where questions as to the cost of raw materials, fuel, and freight are of deciding importance. The present unhappy state of Europe, causing a shortage of many drugs and chemicals, has brought this control home in an unmistakable way to the public, who have been made to realise what the manufacturers have known and ignored for at least a generation. Needless to say, there have been many meetings to discuss the situation by those more or less directly affected. The Society of Chemical Industry, both at their headquarters in London, and at several branches, have dealt with the matter, and Dr. Mollwo Perkin has recently read a most interesting paper on the "British Artificial Colour Industry" before the Society of British Dyers and Colourists. I labour, therefore, to a certain extent, under disadvantages, particularly as this manuscript had to go to press before I had an opportunity of learning the particular aspect of this important subject to be touched upon in the paper read here last week by Sir William Tilden. From a conversation with Sir William Tilden it was possible to gather that there was bound to be a certain amount of overlapping; but the general feeling seemed to be that the subject was of sufficient importance to justify a little redundancy, which, at the worst, would only serve to emphasise the need for action. Needless to say, numerous committees have been formed by all sorts of societies and groups of people more or less directly interested. To the lay mind such committees are places where people go to recite speeches, and they naively assume that the speeches are useful and have a purpose. This is quite a usual conception of a committee; many committee men share it. In times of stress such as those through which we are living, it is increasingly difficult to consider such questions as the one before us to-night from a detached and abstract standpoint. Within the bounds of the Chemical Society, which has done so much to advance science and industry, and has taken the best that could be offered by people of many nationalities, we can at least endeavour to remember that the marvellous and complicated structures of science and industry are international, that in their essence they know no country; that they stand or should stand as one indissoluble link binding all humanity into one great whole. Attempts, and I think foolish attempts, have been made to allocate to various countries the services which they have rendered to this particular aspect of the progress of humanity. It seems to me quite impossible, even if it had any value, to attempt such allocation. Pure science and industry are so interwoven in as far as they make for material progress that they cannot be considered apart. The apparently unimportant pure scientific discovery of to-day becomes the great cornerstone of an industry to-morrow. Those who adapt scientific discoveries to industrial use are as entitled to honour and reward as those who made the original discovery. Just as the progress of pure science is largely limited by the nature and accuracy of the instruments available, so industrial progress is limited by the nature of the machinery available. Those who discovered the spectroscopic little thought of the enormous field of investigation to be opened up by it; those who discovered the possibility of making fire and acid resisting vessels of pure silica rendered possible manufactures which the last

\* Read before the Royal Society of Arts, December 2, 1912.

such vessels had hitherto prohibited. The immediate material benefit derivable from the discovery of new means of industrial attack may far outweigh that from theoretical discoveries which have cost infinitely more of attainment. At a recent meeting of the Society of Chemical Industry in London, where some of the views put forward were characterised as puerile in a chemical trade paper, one speaker referred to the futility of looking at the past, as the present was decidedly a time for action. This is a characteristically British attitude. The time for taking action is exactly the time when the closest regard should be paid to the warnings and lessons of the past. The laws of cause and effect which are studied so earnestly in natural sciences, apply with equal certainty to the more complex relations of human economics. A study of the vast literature of this country would be more than sufficient to convince anyone of the reckless manner in which the literature of our own country is neglected. This being the case, it need not surprise us to find that the scientific and technical literature in foreign languages seldom receives consideration.

We will, then, presume to ignore the advice so proffered, and will take a rapid glance over the progress of scientific and industrial development in Germany and at home. It is probable that the laws relating to the influence of environment, which have been proved to be so important in the animal and vegetable world will be equally applicable to the development of industries, save that influences, such as national temperament, education, and financial relations of a complex nature, have to be brought into consideration. Industrial development on a very large scale was first rendered possible by the introduction of the steam-engine as a power generator and the provision of adequate means of transport. At a period during which this development was taking place here, the rest of Europe was in a sufficiently unexcited state to permit of this country, without serious opposition, becoming the workshop of the world. No licence was required to sell the output of our mills and our ironworks. America, like a healthy growing child, had an insatiable appetite for all those finished and intermediate products which could only be produced by a nation whose industries had been slowly developed and well established. In those days the English manufacturer, who paid low wages, and exacted long hours, made enormous profits. The experimenting, which had to be done to develop the various industries was of a rule-of-thumb character and essentially non-scientific in its nature. Probably no nation is so well fitted as the Anglo-Saxon race to develop rapidly along such lines. As a race the people are practically incurable, and so long as development required nothing more than the closest application of a healthy common-sense, progress was amazingly rapid. A very old man, whose family was one of the earliest to take up the manufacture of cast steel in this country, has told me that in the early days of the firm's history it was no uncommon thing to receive orders for tons of steel required for the manufacture of drills and tools to open up the virgin wealth of America, in which not only was no price mentioned, but it was explicitly stated that within the bounds of reason quick delivery would compensate for any price. The products of our boiler yards were famed throughout the world, and incredible profits were made by firms whose successors have found the competition of recent years more than they could support. This was, of course, due to the fact that in the days of prosperity the profits were divided to the last penny, the machinery was allowed to get out of date, and the working people refused any longer to play the part assigned to them by the manufacturer in his profit-making schemes. Dr. Mollwo Petkin has probably given the correct explanation for this pronounced tendency of British manufacturers to starve and bleed their own business. The rapid industrial development of foreign countries called for enormous capital for railways, shipping, docks, and harbours, and the opening up of mining and agricultural properties, and it was felt that a better return could be obtained from such

ventures. English spinners and weavers were supplying the whole world with their products, while loom and mule machinery makers were working day and night to supply these foreign purchasers with the machinery for their infant industries which were in future years to compete with the home country for their own and neutral markets. For close upon 200 years the tide flowed in our favour. There was no necessity to practise economy. Nature had been lavish with our raw materials, our inland position and the proximity of our manufacturing capital to the sea-board gave us natural advantages which, added to a favourable situation in international relations, rendered the growth of our material success inevitable. To the thinking mind, it was obvious that such a concatenation of favourable circumstances could not continue indefinitely. We provided other countries, at great profit to ourselves, with all the means necessary for competing with us in those markets in which we had hitherto enjoyed a practical monopoly. Our own works were frequently equipped with out of date machinery, which was busily employed in making more modern plants which were put into the hands of those who realised that they would have to exert their powers to the utmost if they were to gain a fair share in the barter of the great international bazaar. The British industry of to day is in the position of a son inheriting an established business, and having in addition a very large income derived from the labours of past generations. Properly used, such a situation should make for enhanced prosperity; but even such powerful advantages may be nullified if the effort to work along the lines which proved successful in our grandfathers' days are continued too long. Capital directed by ignorance and apathy cannot hope to compete for ever against the forces which are brought to bear to-day.

The industrial life of Germany may be said to have commenced little more than a generation ago. To all intents and purposes an inland country, with little sea-board, they were under a huge disadvantage in every department which required raw materials obtained from abroad. In many directions their natural resources were comparatively poor. They had no iron ores which were comparable with the hematites of Cumberland, their limestone was largely dolomitic, their coals were for the most part poor in quality, and lay often in distorted seams, more like those of our Bristol coalfield than the comparatively easily-worked deposits in our northern area. It was recognised at an early period in their industrial development that national progress in a country situated as was their own could not be left entirely to individualistic effort. Nationalisation of railways and canals became an obvious necessity if differential traffic rates were to be allowed, and this was the first step towards the nationalisation of the German economy. Far from the sea-board, the German manufacturer was at a disadvantage in the far-sighted way in which every problem of commerce and industry in Germany is regarded from a national standpoint. It is realised by everyone that individuality must be, to a certain extent, fettered for the benefit of the nation as a whole. In this country individuality runs rampant, and except in times of stress, such as those through which we are passing, the national or imperial bearing of any individualistic action receives not the slightest consideration. The very people whose fathers sold land to the railway companies at absurdly inflated prices now complain that, owing to the high railway freights in this country they cannot make adequate profits from the investment of the money obtained from these same companies by an earlier extortion. No doubt many of those who have made their profits from such action would like to see the English railways nationalised and freights reduced at the expense of that patient beast of burden, the British public. Whereas Germany is continuously developing her network of waterways, we in this country, with a customary lack of national forethought, allowed our waterways to become controlled by the railway companies.



Having thus settled the enormously important question of transport, Germany had to consider the lines along which she should seek for an expression of her industrial destiny. Agriculture, there as here, the largest individual industry, received attention which is as striking as is the lack of it in this country. Proper afforestation schemes were rendered compulsory; enormous areas of land fit for little else were put under potato cultivation, and science was called in to help to create a new outlet for the crops. Germany became essentially the starch, glucose, and alcohol producing country of Europe. Other large areas were used for the cultivation of the beet, and once again science was called in to assist in the disposal of the roots as raw materials for the production of sugar. If the manufacturing of iron had to become a great industry it was necessary to develop economic methods for the utilisation of the great deposits of low-grade phosphatic iron ores which were those chiefly available. In addition to the home deposits of iron ore large amounts have been imported, but how successfully the problem has been tackled is shown when we consider that twenty years ago the German production of iron was a mere fraction of our own, whereas to-day the German output exceeds the British by nearly 200 per cent. The problem of working up the complex metallic ores has fallen almost entirely into German hands. They alone were willing to spend the time and money necessary on researches pertaining thereto, and they alone seemed willing to devote that close chemical skill and attention which is necessary in dealing with these complex problems. In the early days of the chemical industry it must have been quite evident that Germany could not hope to compete in those branches of heavy chemicals such as soda ash, caustic soda, sulphuric acid, bichromate of soda, alum, &c., where cheap raw materials, freights, and cheap fuel play a greater rôle than chemical skill and complex machinery. There is, however, not the slightest doubt that Germany realised years ago what this country has not yet grasped—namely, that all industrial development tends to become more and more scientific. The adequate utilisation of the by-products from an industry may settle the question of the survival of the industry itself.

The necessity for broad co-operation in great industrial problems was recognised and acted upon in Germany in a hundred directions. By-product recovery coke ovens were installed in the immediate neighbourhood of the blast furnaces, and the surplus gas from both was used for power generation. The steel works were erected in the immediate vicinity of the blast furnaces, so that the surplus power might have an outlet. Where it was impossible to bring the steel works to the vicinity of the coke ovens and the blast furnaces, the surplus energy from these was transmitted far and wide in the form of high-tension electric current sold at an astonishing low price and thus tending to the introduction of new small industries within the immediate area. The by-product recovery coke ovens were regarded as another end, but surely Germany had been developing her fine chemical industries, dyes, and even. Many of these manufactures were dependent for their raw materials on products only obtainable in Germany from this country. We have been building up an enormous industry, not only in the spinning and weaving of cotton and woollen yarns and fabrics, but a correspondingly great industry in the bleaching, dyeing, and finishing of these products. This has been chiefly developed on dyes obtained from Germany, but while we have been content to leave ourselves entirely in the hands of others, the Germans have, by the methods of scientific skill and a sensible use of capital, rendered themselves independent of this country. German capital was spent the more to foster the development of by-product coke ovens and the development of the blast-furnace trade in the production of suitable apparatus, to the end that twenty years ago practically the whole of the hard coke produced in this country was made to give up its toll of by-products which were the raw materials for vast quantities

chemical industry. It was in Germany that the preliminary treatment of low-grade coal to render it fitted for the manufacture of a suitable blast furnace coke had its origin and development, and only in the last few years have our colliery companies recognised the value of adequate sorting and washing plant in connection with their output.

The history of the growth of the phosphatic manure trade was a striking lesson in German adaptability, but the time at our disposal will only permit of attention being called to it.

In the whole history of human development, perhaps no trade has varied less in its methods than that of the potter, and so long as this manufacture depended primarily on the proper utilisation of raw materials as found in Nature and great personal skill on the part of the work-people, so long did this country control the industry. Favoured to an extraordinary degree by Nature in the provision of the necessary raw materials, our work-people developed an almost unnatural skill for the production of beautiful objects under the most adverse conditions and with the most primitive mechanical help. The discovery of the possibility of casting complex forms and the growth of the electric industry with its great demand for porcelain of high insulating capacity, opened the door to German competition, until, before the war, it could be said that the world's demand for electrical porcelain was practically met by Germany alone. The sanitary ware trade has been for many years in Europe an English monopoly, probably largely owing to the lack of suitable raw materials in other countries, but by an expenditure of hundreds of thousands of pounds this situation has been changed, and had Germany at the command of its military dictators, not entered upon this war, I am confident that the control of this industry would have fallen into German hands in the very immediate future.

At the recent meeting of the Society of Chemical Industry, above referred to, Professor Henderson referred to the chemical industries of Germany as being merely the development of the crumbs from the British loaf with which they had had to content themselves. In so far as the metallurgical industries are of necessity chemical industries, the term crumbs, as applied to our iron and steel trade, must be greater than our own, seems out of place, and the remark is only another unfortunate example of the wilful blindness that exists in many quarters in regard to an already too strongly developed feeling of national self-esteem. The British as a nation have always been so favourably situated that they have been able to grow with difficulty. As a race we are a nation of which we can be justly proud that it is a little less than treason when those to whom the people should look for guidance and warning feed their ears with some flattery and lull them to continued sleep with mental opiates. In ever-increasing degree, both in this country and Germany, the population are dependent on the machines for their livelihood. Both countries have long passed the stage at which their home market is capable of keeping the machines occupied in full activity. In addition to each being the time a large customer, both have to look to the rest of the developed parts of the world for an additional outlet. Someone has said that a nation like the newspaper is a creature of its own making, by which is meant in some measure that the first few years of its life are spent in the shape of a child, and that the rest of its life is a matter of ever increasing maturity. Our own smaller population has on the whole been equally well fed during the same period, and yet we have seen there was a possibility that a large proportion of the larger nations could be taken in a small country whose work was done in a small part, well and profitably done, and whose industry is expressed in the sleekness of the German capital and the war of the



growing number of industries in this country. I have not seen that any serious attempt has been made to the much more serious end of discovering why the Germans should desire or should be able to get such a foothold in this country. In some few instances I could supply an answer from my own experience. We have already seen how the German Government bring science and agriculture to work together in afforestation, and the cultivation and utilisation of potatoes and beetroots, but throughout the German national history the government have recognised that, as a people, they are in ever-growing degrees forced to live on industry, and that modern industry is built on the hand-in-hand co-operation of science and capital. This country is dependent upon industrial development for its very existence in a higher degree than Germany, and yet so far as governmental assistance or interest is concerned the principal occupation of the British people might be the signing of dividend coupons. The German Government is incomparably poorer than our own, and yet the financial assistance which they render to technical education is immeasurably greater. The standard of general education is undoubtedly higher, no doubt largely in consequence of the temptation offered by their one-year service system in the army to those who have passed a certain high standard of efficiency. In a land where the standard of payment is, on the whole, much higher than our own, the leading men of German technical schools are far better paid than in this country. The heads of the technical school staffs are encouraged to become acquainted with the latest technical progress. It is fully realised that a purely academic teacher cannot turn out first-class technical men. The technical industries in Germany attract the best of the staff, the members of the staff are encouraged to carry out original investigations, and the technical staffs are paid a high salary, to be reckoned by some technical industries at a later date at a still higher salary. It is realised that a man, who has work experience as well as technical knowledge, is worth far more to the nation as a teacher than in a private capacity. If an industry requires to make use of ingredients such as alcohol and ether, which are under excise control, the government will go to the greatest trouble to arrange matters in such wise that no needless restraint is imposed. That the staff of a government department should interpret a government order in an unduly restrictive sense, so that an industry might thereby be hampered, is there inconceivable. Only in Great Britain and Turkey are government restrictions allowed to be interpreted at the will of the permanent officials. I do not for one moment wish to imply that I consider that the question of industrial alcohol has been, of the main, or even of serious import, compared with others, in our neglect of the fine chemical industries. I quote it rather as an example of the contemptuous attitude which our government has hitherto adopted towards matters industrial. In certain branches of the chemical trade it is essential to have the chemically-pure alcohols and ethers, but the would-be manufacturer is told, by the Government, in effect, that he is not to be a judge of what is necessary, but that the question will be settled by some heaven-sent genius in their permanent employ who, like the journalist on a halfpenny paper, knows more about the subject than the man who has made it a life's work.

A feature of the German industries is their willingness and ability to work in co-operation, as is shown in many ways which are no doubt familiar to most of you, but with which we have not time to deal. With all the help which a favourably-inclined government could render, the German industries would have been unable to approach their present standard of efficiency had it not been for the remarkable co-operation which takes place between science and capital. This can perhaps be best illustrated by means of some concrete examples. Let us suppose that some chemist in Germany has discovered a new and cheaper method for making some chemical product which

is in considerable demand, or which might become a large article of manufacture if the price were sufficiently low. If the manufacture is likely to require a considerable capital the inventor would probably go to one of the large banks. The German banks permanently retain the services of some of the leading authorities on a wide range of subjects and the inventor would be asked to put all his case before the particular expert in charge of his department. If the report were of a sufficiently satisfactory nature on the scientific side, the bank would proceed to make their own inquiries, through the many channels open to them, as to the probable outlet for the new product. If the outlook were in all respects sufficiently satisfactory, they would advance the necessary capital at a reasonable rate of interest, making certain stipulations such as that the business should be carried through their bank; that payment for the finished products should be made through the bank; that no contract for the sale of the finished product should be made with any firm without their consent. The bank having made these facilities for running the business, the inventor would be asked to give up this wise position, and to become a partner in the business. We have presumed a case in which the inventor has some knowledge which is worked out to commercial feasibility, and capable of being demonstrated to an adequate extent on an experimental scale, but the activities of the German banks do not by any means cease at this point. An inventor may have made certain discoveries in a new or valuable line of work which, on the small scale, or with the assistance of the disposal of the inventor, cannot be demonstrated commercially. It may only be possible to show that with the expenditure of considerable capital and much labour and time great results be expected. If the new discovery adumbrates great commercial possibilities, such as the development of a new industry or means for obtaining control of an existing one, then the banks are willing to give assistance on very reasonable terms.

Naturally, in the latter case the bank makes the most diligent investigation by means of their own experts, and by calling in the aid of any of those likely to be best qualified to help in coming to a decision as to the probable economic value of the principles foreshadowed by the new work. The committee of experts may say that what has been put before them is a new invention; that it seems to open up possibilities that by its help certain great industries of world-wide importance, at present carried on by slow and expensive means, may be entirely revolutionised, and that which took days may be done in minutes, or that which employed expensive materials may eventually be done by employing cheap residual products. They may admit quite candidly that, although all this is likely to be none the less problematical; but still, in their opinion, in a few years' time, and the expenditure of £200,000 or £300,000 will, under the best of circumstances, be in a situation which will enable them to exact very great returns for their outlay. The writer knows of a very apposite case, where a company has been formed, with a capital of nearly half a million sterling, to develop certain inventions which in many directions were very embryonic. Practically the whole of this money has been provided by private and other banks, who realise that quite a number of years may elapse before an adequate return is gained, but they also realise that, so far as human skill and knowledge can foresee, a few years will place them in a position to control several of the world's greatest industries, in which case their return will be of a very high order.

Again, nothing is more startling to the Englishman than the ease with which one can gain admission to those in command of the great industries. The directors of the German companies, for the most part, and the managing director invariably, are men of high technical skill in the business they control. The idea of putting a stockbroker or a retired army colonel at the head of a scientific industrial concern would be regarded as an act of madness. Not only are German businesses run by men who understand them, but these industrial leaders have always time

to give adequate consideration to any new proposal which is brought before them. It would be the exception rather than the rule to find directors in an English company who were capable of appreciating, still less of judging, the merit of a technical point relating to their own business. It would be almost an impossibility for an unknown outsider to obtain admission to such directors, and even if the unknown inventor succeeded in getting within the veil which hides the holy of holies, it would probably be to find that the master-mind had so many appointments that he never by any chance had time enough to consider any proposal thoroughly. The heads of a German concern have always time to look thoroughly into anything which interests them; they are sufficiently technical to realise the necessity for going into details, a work experience having taught them that it is on details that great processes come to grief. In spite of their intellectual and commercial attainments, however, these directors are, in some respects, both modest and unassuming. They still think that success can be purchased only at the cost of labour; they are content to work from 8.30 to 6.30, with two hours' pause in the middle of the day, and they work full six days to the week. No doubt they envy, but they do not lay claim to, that super-type of intellect which, labouring hard from eleven till four, with an interval for rest, sometimes even five days a week, expects, not only to retain its old position, but to dispossess its competitors; they even learn foreign languages, so that they may profit by the knowledge gained by other people in other countries.

Let us suppose for one moment that it was Germany that was short of drugs, photographic chemicals, and dyes, and that England had possessed a monopoly in these products. Further, we will suppose that the joint general manager and head chemist of one of the large English drug and photographic chemical works had found himself in Germany at this period. With sufficient acquaintance in that country, men with whom he had for many years made large contracts, and who were fully cognisant of his scientific and technical ability to guarantee his claims. He could go to any bank and say, "I can show you how to make a number of photographic chemicals and drugs even more cheaply than they can be made in the country which has hitherto controlled the manufacture, because you have the necessary raw materials, because you have, indeed, previously sold these raw materials to the previous makers. I bring you the necessary evidence that these products can be made at half the cost, and, therefore, before the war, and I can show you that the same is true of our own and neutral countries of these products, and that some thousands of tons per annum, and that, under normal circumstances, after the war is over, it will be impossible for your business to be displaced by undercutting. Finally, I will bring you reputable dealers who will make contracts for hundreds of tons of these products at prices which will pay for the plant and show profits in one year's working." The bank would commit these statements through their experts, and probably within forty-eight hours all the money that was required would be available at 7½ per cent. The man who possessed the scientific, technical, and commercial knowledge would thus be enabled to build up a business which would be profitable and valuable to the community, the fact being that it is recognised in Germany that capital is entitled to a fair return and nothing more.

Now let us imagine that circumstances were reversed. It would require the capital of a British banker to depict the scene in the board-room of an English bank where such a proposal had been made. One can imagine the amazement of such knowledge relating to technical chemical work. It being presumed that a travelled and educated individual, as would rather than our so-called chemists, would not, for the most part of the job and the money, be so ready to say, that the bulk of such business should be left to the experts for dealing and other things, and that the bank should not be concerned in such a matter.

weed-destroyers. He would discover, if he ever got a hearing, that the larger chemical works, cognisant of the mental attitude of the financial classes in their own country, would either refuse to put forward the necessary capital or would offer to undertake the manufactures on utterly impossible terms. Everywhere he would make the, to him, astonishing discovery that no one realised the possibilities of the industries which he wished to develop. Drugs and photographic chemicals were sold in ounce bottles. If he endeavoured to prove that the total trade in photographic developers was in the thousands of tons per annum he would be met by polite incredulity. Eventually we may suppose that our hero decides to test his fortunes at that great hub of cash, intellect, and roguery—London. Guided by past experience he would probably manufacture a few of the products under the observing eye of the finest independent expert he could learn of, in a country practically ignorant of the industry which he represented, and he would obtain from men of standing the offer of contract for tons of the materials he proposed to manufacture showing very great profits. If a stranger to the city, the odds are a hundred to one that he would fall into the grasp of some plausible tout of a third-rate company promoter, in which case, unless we are in for the second edition of a thirty years' war, his chances of arriving at any finality are practically nil. The best that he could hope for would be to become a paid servant of a heavily watered company, short of working capital, loaded down with preliminary expenses, weighed with directors and a staff not only ignorant but careless as to the future of the concern. The amount that he himself might hope to receive from this last and greatest evidence of twentieth-century progress, a city company promotion, would be little else than paper. He would learn that the cash consideration exacted from the British public on the strength of a prospectus backed by guinea-pig directors was required, as to the greater part to pay commissions to a long train of intermediate parasites who live in this wise on the spoliation of industry.

If by a miracle he succeeded in escaping the clutches of the type above described and was brought into direct touch with real capitalists, he would learn, in a practical way, the immense respect exacted by English capital, and would be astonished to find that as a representative of creative and productive industry he was to be treated as a lower organism which should be devoutly thankful for being allowed to exist on terms with less intellectual but more material requirements. He would find that the same which representatives of the golden calf had no time to go into details. Having assured themselves that there really were considerable prospects of large financial returns, the last thing they desire is to permit the inventor to put himself in a position to demonstrate the full value of what he is selling.

Whatever certainly attaches to the processes of which he is a master, he must be made to feel that they are nothing more than a vast experiment. Having a positive contract for us say for forty tons of a special product showing profits of 35 per cent, and having demonstrated by means of an independent expert appointed by themselves that he can make the product at something like 1s. per lb., they will probably look to find him a very inadequate capital for which they will require a still cumulative preference interest, and the bulk of the profits remaining beyond that. In his own country, where salaries ruled lower, he would have received at least double the salary that he will now receive. No doubt the wanderer from another country would think these terms sufficiently onerous as they stood, but he has yet to learn that in a hundred and one ways his diminished rest of the profits had to be the scantiest. At the wisdom of the directors other chemists can be put in over his head. For what is a director if not to find comfortable berths for striving relatives? The men of gold will employ a learned advocate, who will draw them up memorandum and articles of association most cunningly worded,

whereby, should the occasion warrant it, they can issue shares at a discount, or bring out new classes of shares having prior rights; where they can, in effect, render it practically impossible for any serious proportion of the profits to wander in undesirable directions. Should the inventor have the temerity to suggest that such terms would be hard if applied even to untried inventions which had still to live through that development period where childhood diseases are active, recourse would be had to the worst effects of example. The ocean of commercial history is foul with the carcasses of dead and gone companies for untried chemical and quasi-chemical inventions, and one or more of these would be gibbeted for his benefit. Of course, he would not be given time, even if he had the necessary knowledge, to find out whether the company in question failed because the process was intrinsically bad, or whether, which is much more likely, it perished from that frequent disease of modern limited companies—water on the brain, or rather water in the shares. In my opinion the modern company law, with its attendant train of parasitical followers, is more responsible than anything else for the failure of scientific industries to advance in this country. The longer I am acquainted with the men who are something in the City, the greater is my respect for the workers of the North. Just before the war broke out I had almost completed negotiations whereby it would have been possible to introduce selected British inventions to a powerful group of German capitalists. It had long been obvious that it was a waste of time and energy to endeavour to get these, even intelligently considered by English manufacturers or English capitalists. It proved possible to do more business in this direction in one week in Germany than in this country in a year. In many cases the German capitalists insisted upon having the right to acquire the English patent along with the German. They knew that England was a great market, and much the nearest centre of banking up an export trade; they also knew from past experience how small were the chances that they would have to meet any competition in this country. They had found from past experience that it was useless offering their inventions on this side of the water, and in a large and ever-growing number of cases, convinced of the great value of the processes they were exploiting, they actually bought controlling interests in English companies in order to be in a position to force these to take up new methods which were vital to the progress of the industry in question. If a German discovers a new method for increasing the yield and cheapening the cost of a chemical substance which is an intermediate product in the manufacture of other intermediate products eventually used in dye-making, we cannot take on the manufacturers ourselves, for it is useless. Our chemical works are so far underdeveloped in certain directions that they have no use for such a product. It is about as useful as an improved watch escapement would be to an Esquimaux. If the German starts a works in this country for making this and other products, or if he purchases a controlling interest in a firm with the object of compelling its manufacture, we complain of German dominance in our industry. The German commercial man was likened in this room to a burglar, and this because he visits our manufacturers in the middle of the day and finds them asleep. Modern commerce is warfare, and the weapons employed are—inventions, tireless industry, skill, and capital. We make the mistake of putting the last first. Those who do research and make inventions, whether in chemistry, engineering, or any other branch, are the yeasts which leaven the whole mass, but in this country we do not allow those conditions of warmth which permit the yeast to work. Gold in itself is not nearly so valuable a metal as iron, and we are slowly but surely finding out that capital itself is an over-valued possession if it be not used for the benefit of the industries and consequently of the nation as a whole. Our men at the front in defence of British honour and British security are risking their lives, but the English capitalist has no desire to risk

anything. Having, through his own sloth and apathy, through his unwillingness to look ahead, through the inability born of ignorance to appreciate the right use of science, fallen behind in the race, he now desires protection. He would persuade the British people that representative government means government of the people, by the people, for the benefit of the manufacturer. He is a veritable dog in the manger. He refuses to take up new processes or to apply new methods, and objects still more when others, with greater enterprise, seize the opportunity. If the greatest war, if the greatest opportunity this Empire will ever know will not move him to action, I am not so conceited as to imagine that any dialectic weapon which I can wield will be sharp enough to penetrate his hide-bound self-complacency, still less the triple brass of his imagined self-interest.

### LICENCE TAXES AND COMPANY LAW.

A meeting of the Imperial Advisory Council of the Institute of Industry and Commerce was held on December 28, 1914, at their offices on Aldwych St., London, for the purpose of considering the best means of approaching the various Dominion Governments with a view to abolishing the payment of Licence Taxes payable by British commercial travellers in the Dominions and Colonies, and also for the purpose of considering the best means of bringing about the standardisation of Company Law throughout Great Britain, the Dominions, and Colonies, in order to facilitate commerce within the Empire. After carefully considering the proposals, the Council decided that a Memorandum should be drawn up by the Institute after consulting with the leading specialised trade organisations, and that this memorandum be submitted to the Agents General of the Dominions and Colonies for submission to their respective Governments.

It is gratifying to learn that both suggestions were sympathetically considered and that everything possible will be done to straighten out any inequality that may be prevalent in Company Law and with regard to Licence Taxes payable by British commercial travellers travelling in the Dominions.

Should the Committee be successful in accomplishing the objectives aimed at—and it looks as if it will be possible—it will have performed a very considerable service for the industry and commerce of the country.

The policy of the Institute of Industry and Commerce is to develop a set of satisfactory working conditions within the Empire in which industry can operate, and if this is accomplished satisfactorily a considerable increase in business should follow.

The Institute continues to receive very distinguished support from among the leaders of industry and commerce.

### CONCERNING GAS FLAMES.\*

FLAME is a very interesting phenomenon when studied scientifically. There are many varieties of flame; to begin with, those that are smoky and those which are not. Our coal fires give out a terribly smoky flame, and thus waste a great deal of the fuel. An old-fashioned fish-tail gas burner does not smoke visibly, but the state of any white ceiling above such a flame shows plainly that it does smoke in reality. It cannot help help doing so, because its luminosity is due to the white-hot particles of carbon suspended in the flame, and these have not all got time, so to speak, to combine with the oxygen of the air and get converted into carbonic acid. Hold a cold white plate above the gas flame, and it is blackened at once by the carbon particles escaping combustion. The Bunsen

\* From the *Pioneer of India*, Nov. 4, 1914. (Written by a Member of the Royal Institution.)



burners used extensively in all chemical laboratories get over this trouble by allowing air to mix with gas just before it is ignited. The combustion of the gas is thus rendered more complete. For that reason it is non-luminous. There are the small carbon particles floating in it, to get hot and give out light, but it is all the hotter for that, because in the process of being properly burned they contribute to the heat of the flame. This is all very elementary chemistry, but it must be borne in mind, if we are to understand a new development connected with the subject of flame which may have a very important bearing on the use of gas, not merely for lighting up rooms, but for highly important industrial operations.

The new development in question is the result of long and patient work on the part of the inventor, Mr. A. C. Bunsen, who has been able to do many better things than most of us. He has been found possible to mix gas with air in exactly the right quantity of air required for its combustion. In this way the mixture is, of course, explosive in the highest possible degree. One cannot see at a glance why such a mixture, supplied through pipes, should not explode back through the pipes and blow up any community rash enough to use it. But before going on to explain how this contingency is averted, let me deal with certain interesting features of the arrangements, accepting for the moment that the explosion difficulty is circumvented.

The mixture combines within itself both the combustible and the supporter of combustion. It will burn on indefinitely in a closed vessel, not even incommode, by its own products of combustion. I have seen this proved (at the inventor's laboratory) by an extremely pretty device. A transparent tube, looking like an ordinary glass test-tube, but really made of the all-but infusible silica, now so great a blessing to the chemist, is held up inverted in a frame. A fine silica tube carrying the self-supporting mixture is lighted and put up inside the inverted tube, which, of course, is closed at the top. The minute colourless flame burns within half an inch of the top, and then, as the whole arrangement gets hot, apparently goes out. But one sees by the intensity of the heat maintained that it has not really gone out. It has simply subsided into the condition of perfect combustion, which does not express itself in a flame at all. Perfect combustion, in fact, is an invisible process, or one that only betrays itself by generating intense heat, which has the usual effect on bodies in the neighbourhood of making them visible enough; intensely incandescent, in fact, they can bear heat without sustaining fire. With the flame that burns but does not burn, in other words, wasteless like sunlight.

This flame which you cannot see is a curiously fascinating spectacle—to put the idea paradoxically—for anyone who appreciates its scientific significance. And the experiment with the silica tube is significant in another way. That confined space must obviously become filled at once with the products of the combustion going on—CO<sub>2</sub> and H<sub>2</sub>O. That does not interfere at all with the comfort of the invisible flame, and the products in question are simply driven down as they accumulate. Perfect combustion, in short, does not require a chimney, only a drain pipe to carry off the H<sub>2</sub>O. No such wholesale precaution is required when the new self-supporting gas is simply used for domestic illumination. In that connection the invisible flame is employed to heat an incandescent mantle, and it does so much more effectively than the ordinary Bunsen flame now used for that work. But the big, important application of the new process has to do with furnace work. Applied on a large scale to the work of heating crucibles, the results are very striking. Any given quantity of gas does as much more work when burned as a self-supporting mixture than it does burned in the ordinary way, that the economy is something like 40 per cent. And many factories concerned with melting metal use gas furnaces; so that there seems to be an important practical feature for the inventor to have been describing.

But we must now deal with the arrangements that pro-

vide for the safety of a system that at the first glance seems equivalent to a proposal to use gunpowder as a new kind of fuel for fire grates. The rate at which explosion waves travel through pipes has been long under investigation, and a pressure that is not at all excessive for gas lighting purposes would exceed the rate at which explosion waves start. But pressure may vary. It was obvious that the new system could not rely on pressure alone. Elaborate experiment has shown that there is a way of baffling the explosion wave. If just behind the burner, the flow of the explosive gases is interrupted by a flat disc of small diameter, round the edges of which the gas has to pass, no explosion wave will ever get back beyond that obstruction. The aggregate sectional area of the crack round the disc must be just equal to the sectional area of the pipe conveying the gas, but that condition once established the explosive gas may, it appears, be burned with perfect safety. The disc need not be very large. For a quarter-inch tube, conveying enough gas mixture to heat up a mantle giving 160 candle-power, a disc only one and a quarter inch in diameter is enough to baffle explosion. With a half-inch pipe, such as would be required for a gas fire in an ordinary room, the baffling disc would be three inches in diameter. In the case of large gas furnaces no such arrangements are required, because the gas and air are only mixed just before the place of ignition. In order to keep the mixture just right a device is employed which could not be explained without diagrams. Enough to say that it depends upon balancing the respective pressures of gas and air, so that the character of the mixture, as delivered at the place of ignition, is always the same.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, November 19, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,  
in the Chair.

THE PRESIDENT mentioned, with deep regret, that Mr. John Gunning Moore Osborn, of Gains College, Cambridge, who was elected a Fellow on June 27, 1909, had been killed in action on August 27.

It was announced that the Council had passed the following resolution:—

"The President and Council of the Chemical Society, at their first meeting of the Session, desire to be associated with the statements and opinions set forth by certain scholars and public men in their manifesto published in *The Times* of October 21, 1914."

It was also announced that a Research prize of the value of £200 has been placed by Sir Robert Hadfield, F.R.S., Past-President of the Iron and Steel Institute, at the disposal of the Council of that Institute, to be awarded by the Council to the author of the best contribution to the publications of the Institute on the subject of the "Different Forms or Combinations of Carbon in Iron, Steel, and Alloys of Iron with other Elements." Competition for the prize is open to metallurgists, chemists, and others interested in metallurgy, and it is proposed that the prize shall be awarded at the Annual General Meeting of the Institute in May, 1915, for the best paper presented before February 1, 1916.

Intending competitors are requested to communicate, in the first place with Mr. G. C. Lloyd, Secretary of the Iron and Steel Institute, 28, Victoria Street, S.W., from whom further information may be obtained.

Certificates were read for the first time in favour of Messrs. Frank Buckley, 10, Berry Street, Greenfield, Oldham; Reginald Robert Kintson, Grammar School,

Ipawish, Queensland; Harry Shulman, 21, Tredegar Square, Bow, E.

A certificate has been authorised by the Council for presentation to ballot, under By-law I. (3), in favour of Mr. Thomas Clifton Hurford, Phuket, Siam.

Of the following papers, those marked \* were read:—

277. "Studies in the Camphane Series." Part XXXVI. N-Chloroaminocamphor." By MARTIN ONSLOW FORSTER and MAX SCHLAEFFER.

N-Chloroaminocamphor,  $C_{10}H_{17}ClNO$ , prepared by adding alkaline chloroamine to aqueous aminocamphor hydrochloride, crystallises from petroleum in colourless needles melting at  $43^\circ$  and decomposing at  $85^\circ$ ; it liberates iodine from potassium iodide, and regenerates aminocamphor with sodium sulphite. The dry substance rapidly changes into a honey-like mass, losing chlorine, and solutions in benzene or petroleum quickly deposit aminocamphor hydrochloride and contain the anhydride of cyanolauronic acid. In acetone it also gives aminocamphor hydrochloride along with a compound,  $C_{10}H_{15}ON$ , melting at  $155^\circ$ . Ammonia converts it into iminocamphor, and ammonia is oxidised to azobenzene.

#### DISCUSSION.

Prof. GUNTER suggested that camphorylhydrazine might be obtainable either by treating chloro (or bromo) camphor with hydrazine, or by the action of dry ammonia gas on N-chloroaminocamphor in a non-aqueous solvent.

278. "The Dissociation Pressures of Alkali Bicarbonates. Part II. Potassium, Rubidium, and Cesium Hydrogen Carbonates." By ROBERT MARSH CAVES and HENRY JULIUS SACCOMA SENE.

The dissociation pressures of the hydrogen carbonates of potassium, rubidium, and cesium have been determined by means of the apparatus formerly employed for sodium hydrogen carbonate (*Trans.*, 1911, xlix., 1359), and curves have been drawn which accord with the formula:  $\log p = a - b/T$ . The values of the constants are:—For  $KHCO_3$ ,  $a = 10.832$ ,  $b = 3420$ ; for  $RbHCO_3$ ,  $a = 12.712$ ,  $b = 4300$ ; for  $CsHCO_3$ ,  $a = 16.930$ ,  $b = 6300$ . From the values of the constant  $b$  the following heats of dissociation per g-m. molecules of hydrogen carbonate are derived:— $KHCO_3$ , 21,400 cal.;  $RbHCO_3$ , 39,560 cal.;  $CsHCO_3$ , 59,660 cal.

The results of the experiments on the dissociation pressures of the alkali hydrogen carbonates show that not only that the stabilities towards heat of these salts increase with rise of atomic weight, but also that sodium hydrogen carbonate is widely separated from the other three salts in stability. This furnishes another illustration of the fact that a break occurs in the gradation of properties of compounds of the alkali metals at the point of transition from the short to the long periods in the periodic classification of the elements.

279. "The Removal of Sulphur from Silver." By CRELLYN COLGRAVE BISSETT.

The effect produced by adding varying percentages of copper and iron respectively to molten silver containing silver sulphide in solution has been determined.

In the case of iron it was found that ferrous sulphide was formed, the whole of the silver in combination with sulphur being displaced by iron if sufficient for this purpose was added. Ferrous sulphide is insoluble in silver.

Copper was found to behave differently. It was only when a considerable percentage of the copper had alloyed with the silver that the sulphide was removed completely from solution. Even under these conditions the sulphide layer still contained a fairly large percentage of silver.

The results obtained by blowing a current of dry air through molten silver-containing sulphur have also been determined.

280. "Osmotic Pressure of Alcoholic Solutions." By TUDOR WILLIAMS PRICE.

Measurements have been made of the vapour pressure of alcohol and of alcoholic solutions of carbamide and nitrobenzene, of various concentrations, at  $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ ,  $50^\circ$ , and  $60^\circ$  by the air-bubbling method.

The densities were also determined.

The osmotic pressures were calculated from the formula:

$$P - \frac{1}{2}aP^2 = \frac{RT}{V_0} \log_e \frac{p}{p'}$$

where—

$P$  = osmotic pressure of the solution.  
 $a$  = coefficient of compressibility of the solvent.  
 $p$  = vapour pressure of the solvent.  
 $p'$  = vapour pressure of the solution.  
 $V_0$  = molecular volume of the solvent.

281. "The Polysulphides of the Alkali Metals. Part II. The Polysulphides of Potassium." By ALEXANDER RULE.

In continuation of previous work on the polysulphides of the alkali metals (Rule and Thomas, *Trans.*, 1914, cv., 177) the author has investigated the action of sulphur on alcoholic solutions of pure anhydrous potassium hydrosulphide. With varying proportions of sulphur the only polysulphide product obtained was the pentasulphide, which was readily isolated in the pure state. It is an orange-red crystalline compound, melting at about  $220^\circ$ .

By determining the amount of hydrogen sulphide evolved by the action of varying amounts of sulphur on a constant amount of hydrosulphide throughout, it is also shown that the pentasulphide is the polysulphide present in predominating amount in solution.

Considering the results in general, and comparing them with those obtained for sodium, and for rubidium and cesium by Biltz and Dörfert (*Ber.*, 1905, xliii., 53; *Zell. Anorg. Chem.*, 1906, xlviii., 297; *l.*, 67), the stability of the higher polysulphides appears to increase with increase in the atomic weight of the alkali metal. The highest stable polysulphide of sodium is the tetrasulphide. The pentasulphides of potassium, rubidium, and cesium are perfectly well defined, and exhibit an inverse order of solubility with increasing atomic weight, thus coming into line with the platinum chlorides, alums, &c., of the same metals.

No indication of the formation of a hexasulphide of potassium has been obtained in the course of the author's experiments, whereas Biltz and Dörfert were able to show the existence of hexasulphides, both of rubidium and cesium.

The possible influence of the alkali metal on the number of atoms of sulphur taken up to form the polysulphide complex was discussed.

282. "The Progressive Bromination of Toluene." (A Reply). By JULIUS BEREND COHEN and PAVITRA KUMAR DUTT.

In the appendix to a paper on the bromination of toluene (*Rec. Trav. Chim.*, 1914, xxxiii., 183) Prof. A. F. Holleman has thrown doubt on the production of *m*-bromotoluene by the direct bromination of toluene which the authors have observed (*Trans.*, 1914, cv., 504). Prof. Holleman says:—"Il me semble que la preuve que MM. Cohen et Dutt ont donnée de sa présence n'est pas tout-à-fait rigoureuse. Car d'abord ces savants se sont placés dans des circonstances défavorables pour la découverte de petites quantités de l'isomère méta en faisant réagir le brome et le toluène molécule par molécule, ce qui cause la formation de produits bromés supérieurs. Par oxydation ceux-ci donnent des acides dibromobenzoliques qui sont très difficiles à séparer, aussi bien entre eux que des acides monobromobenzoliques. Nonobstant que les savants nommés aient trouvé des points de fusion de l'éther méthylé et de l'acide, correspondant à peu près avec ceux des substances méta pures, cette preuve ne peut donc être regardée comme décisive, surtout parce que ni l'essai de la mélange, ni des analyses ont corroboré ce résultat."

Prof. Holleman's criticism is to some extent justified, although the boiling-point of the mixed bromotoluenes (180—190°) would obviously exclude the presence of dibromo-derivatives which boil at about 240°.

In order to meet this criticism the authors have: (1) mixed the *m*-bromobenzoic acid (m. p. 157—158°), obtained by the oxidation of the bromotoluene by direct bromination, with a pure specimen prepared by brominating benzoic acid (m. p. 157·5—158·5°), and found that the mixture melted at 157—158°; (2) made an analysis of the acid with the following result:—

0·1232 gave 0·1160 AgBr; Br = 40·06.  $C_7H_5O_2Br$  requires Br = 39·8 per cent.

The above affords conclusive proof that the substance in question is *m*-bromotoluene.

283. "Researches on Silicon Compounds. Part VI. Preparation of Silicon Tetrachloride, Disilicon Hexachloride, and the Higher Chlorides of Silicon by the Action of Chlorine on 50 per cent Ferrosilicon, together with a Discussion on their Mode of Formation." By GEOFFREY MARTIN.

The author described a very cheap process of preparing the chlorides of silicon by the action of chlorine on 50 per cent ferrosilicon. He has investigated the most favourable conditions for the action to take place, and described his apparatus, whereby he produced more than 50 kilos. of silicon tetrachloride and 3 kilos. of disilicon hexachloride by passing 150 kilos. of chlorine over about 50 kilos. of 50 per cent ferrosilicon.

The apparatus used for distilling large amounts of the chlorides of silicon in absence of atmospheric moisture was also described.

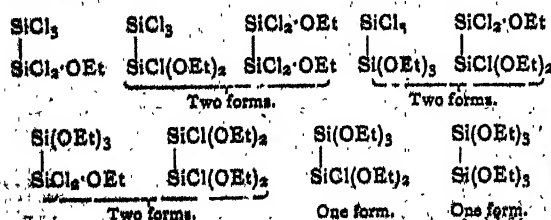
In this process the author prepared some kilos. of the hitherto difficultly accessible and costly disilicon hexachloride,  $Si_2Cl_6$ , and was able to investigate its properties more carefully than has hitherto been possible. He also obtained 180 grms. of trisilicon octachloride,  $Si_3Cl_8$ , and smaller quantities of higher chlorides.

Gattermann and Weinlig (*Ber.*, 1894, xxvii., 1943) attributed the formation of disilicon hexachloride in the chlorination of silicon to the fact that silicon tetrachloride reacted with silicon to produce the hexachloride, thus:  $Si + 3SiCl_4 = 2Si_2Cl_6$ . Experiments were quoted, however, to show that Gattermann and Weinlig were wrong in this, as at the low temperatures employed in the preparation of silicon tetrachloride the latter does not react with silicon to produce noticeable amounts of disilicon hexachloride.

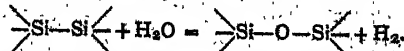
The only explanation that meets the facts of the case is the supposition that in elementary silicon or in metallic silicides the silicon atoms are directly united in chains, and that the first action of chlorine on silicon (or metallic silicides) is not immediately to break up these chains of silicon atoms, but that there are first produced complex chlorinated products still containing chains of silicon atoms directly united. These complex chlorides are then attacked by more chlorine, and decompose into simple chlorides, silicon tetrachloride being thus not the first product of chlorination, but rather the final product.

284. "Researches on Silicon Compounds. Part VII. The Action of Ethyl Alcohol on Disilicon Hexachloride." By GEOFFREY MARTIN.

When ethyl alcohol acts on disilicon hexachloride the following nine substances are, theoretically, capable of being produced, none of which has hitherto been described:—



The preparation and properties of a number of these substances were described. They are all colourless oils, decomposed by water with the production of explosive white hydroxy-compounds, which dissolve in alkalis evolving hydrogen, thus verifying the author's theory (*Ber.*, 1912, xlv., 2097; 1913, xlv., 3289) that in the presence of attached oxygen atoms directly linked silicon atoms are decomposed by alkalis, thus:—



Each direct Si-Si linking thus corresponds with the evolution of one molecule of hydrogen.

The curious circumstance was noted that great cold is produced when alcohol acts on disilicon hexachloride, a vigorous action going on at the same time. Although the first equivalents of chlorine of the disilicon hexachloride molecule are readily displaced by ethoxy-groups, yet it was shown that as each successive chlorine atom is removed the displacement proceeds with greater and greater difficulty, so that the substances  $Si_2Cl_2(OEt)_4$  and  $SiCl(OEt)_3$  are scarcely acted on by ethyl alcohol at the ordinary temperature.

285. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XI. The Co-ordination of the Rotatory Powers (a) of Menthyl Compounds, (b) of the Menthones, and (c) of the Bornesols." By JOSEPH KENYON and ROBERT HOWSON PICKARD.

One "characteristic diagram" (compare Armstrong and Walker, *Proc. Roy. Soc.*, 1913, [A], lxxviii., 388) serves to co-ordinate the rotatory powers for different wave-lengths, not only of *l*-menthol, *d*-neomenthol, and their esters, but also of *l*-menthylamine and its simple derivatives. This method of plotting rotation values fails when the compound contains two possible and dissimilar centres of dynamic isomerism, such as, for example, the menthyl esters of the nitro- and *o*-iodo-benzoic acids and 2-naphthylmenthylcarbamide. The rotatory powers, however, of the menthyl esters of a number of mono- and di-nitrobenzoic acids can all be co-ordinated on another diagram, which differs considerably from that drawn for the simpler menthyl compounds.

The rotation of *l*-menthone and *d*-isomenthone can also be co-ordinated on a characteristic diagram, whilst the same method has been applied successfully to the rotatory powers of *l*-borneol, *d*-isoborneol, and esters of these.

286. "The Rotatory Powers, Refractivities, and Molecular Solution-volumes of Cinchonine and some Derivatives." (Preliminary Note). By DAVID HENRY PRACOCK.

The greater number of the investigations on the connection between rotatory power and constitution have been carried out on esters. Pope and Winnill (*Trans.*, 1911, ci., 2309) examined the derivatives of tetrahydroquinidine and it was thought that a similar examination of cinchonine and its derivatives might produce useful results. The preparation of the acyl derivatives proved, however, exceedingly troublesome. In several cases, even after many modifications, of the method of working, only uncrystallisable gums were obtained. Owing to the pressure of other work this investigation has been temporarily stopped, but the following results are given as of interest.

The examination of the physical expressions for refractivity and optical rotatory power at once shows that there should subsist a close connection between the two properties (see, for example, Wood's "Physical Optics").

Optical rotatory power may be altered owing to a change in the degree of asymmetry of the molecule; for instance, it vanishes when the molecule becomes symmetrical, or by such changes in the internal forces as affect both rotatory power and refractivity; for instance, the presence of conjugated double bonds. Substitution may act in both ways, and by a comparison of its effect on both properties it might be possible to separate these two effects; at present, however, the only means of deducing the refractivity of a dissolved substance is from the value of

$\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$ , deduced on the assumption that the property is additive. In the present experiments the molecular solution-volumes are given, so that allowance can be made for changes in their value when considering the effect of substitution on the molecular refractivity:—

$$\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$$

Benzoylcinchonine was prepared by the usual Schotten-Baumann process. It crystallises in rosettes of small prisms melting at 65° (found,  $N = 7.00$ ;  $C_{26}H_{26}O_2N_2$  requires  $N = 7.04$  per cent).

*m*-Nitrobenzoylcinchonine forms colourless needles melting at 119°:—

0.1507 gave 11.32 cc.  $N_2$  at N.T.P.;  $N = 9.44$ ;  $C_{26}H_{23}O_4N_3$  requires  $N = 9.48$  per cent.

*p*-Toluenesulphonylcinchonine crystallises from alcohol in skew tetrahedra melting at 127°. These are sparingly soluble in alcohol at 25°:—

0.1560 gave 8.06 cc.  $N_2$  at N.T.P.;  $N = 6.5$ ;  $C_{26}H_{28}O_3N_2S$  requires  $N = 6.25$  per cent.

Picrylcinchonine was prepared from the base and picryl chloride. It crystallises from acetone in lustrous golden scales, melting at 180°, and is very sparingly soluble in most organic solvents:—

0.1117 gave 12.70 cc.  $N_2$  at N.T.P.;  $N = 13.97$ ;  $C_{25}H_{23}O_7N_3$  requires  $N = 13.86$  per cent.

The solutions of the above compounds were examined at 25°. The rotatory powers were measured in 2-dm. tubes, the densities measured in pycnometers holding about 10 cc., and the refractivities measured in a Zeiss total reflection refractometer.

In the following table are collected the molecular weights, rotatory powers, refractivities, and solution-volumes at 25° of the above substances:—

Substance.	Concentration, grms. per 100 cc.	M.W.	[M] <sub>0.25</sub>	$d_{25}^{20}$ c.c.	$M \cdot \frac{n_D^2 - 1}{n_D^2 + 2}$
Solvent: Alcohol.					
Cinchonine .. ..	0.6240	294	+138.7°	179	70
	2.8900	294	+135.8°	238	89
Benzoylcinchonine	0.9704	398	+180.3°	329	112
	2.1028	398	+170.7°	320	116
<i>p</i> -Toluenesulphonyl- cinchonine ..	0.5124	448	+17.4°	310	136
Solvent: Acetone.					
Cinchonine .. ..	0.5160	294	+165.2°	249	75
	2.1136	294	+147.4°	244	96
Benzoylcinchonine	0.9448	398	+154.8°	322	91
	2.5280	398	+151.5°	322	89
<i>p</i> -Toluenesulphonyl- cinchonine ..	0.9404	448	+7.1°	342	117
	2.6240	448	+9.4°	354	135
Picrylcinchonine..	0.7132	505	+1968.0°	361	136
	1.2912	505	+1881.0°	356	133

The results show some interesting effects. Like *sec*-butylamine (Pope and Gibson, *Trans.*, 1912, ci., 1762), cinchonine has its rotatory power lowered considerably by the introduction of the *p*-toluenesulphonyl group. The introduction of the picryl group causes a complete change in the sign of the rotation, and also increases the magnitude very considerably. There do not seem to be any details of other cases of the effect of the picryl group, and it is hoped to examine further this behaviour.

Adopting the electronic theory of molecular structure then, the effect of a substitution will be due partly to its disturbance of the intramolecular electrical field of force and partly to the mass of the substituent. If rotatory power is due to vibrating electrons, then the relative effect of these two quantities will depend on the value of  $e/m$  for the vibrating electron, and on the magnitudes of the

changes in mass and intramolecular electrical force brought about within the molecule. This second type of change may be deducible on lines similar to those used by Flürscheim in his applications of Thiele's theory of partial valencies, and has already been examined to some extent by Hilditch.

## NOTICES OF BOOKS.

*The Raw Materials for the Enamel Industry and their Chemical Technology*. By JULIUS GRÜNWALD, Dr. Ing. Translated by HERBERT H. HODGSON, M.A. (Camb.), B.Sc. (London), Ph.D. (Heidelberg). London: Charles Griffin and Co., Ltd. 1914.

The enamel industry has been developed entirely within the last twenty years, and has rapidly become of great economic importance, especially in Germany and Austria. There is no reason why it should not be prosecuted with equal success in England, and the present time offers British manufacturers an excellent chance of undertaking a lucrative enterprise. This book by Dr. Grünwald, who is a foremost authority in the enamel industries, will be of the greatest interest to those who are engaged, or hope to be engaged, in similar work. The geology and chemical technology of feldspars, clays, borax, cryolite, and other raw materials are fully discussed, and detailed descriptions are given of methods of preparation and purification. Statistics of prices, production, &c., and also many recipes for enamels are included.

*Technical Methods of Chemical Analysis*. Edited by GEORGE LUNGE, Ph.D. English Translation edited by CHARLES ALEXANDER KEANE, D.Sc., Ph.D. Volume III., Part I. London: Gurney and Jackson. 1914.

The third volume of this treatise is a translation with some alterations and additions of the third and fourth volumes of the last German edition published in 1910—11. Part I. includes Oils, Fats, and Waxes, Gums, Drugs, Organic Preparations, Rubber, Leather, Tanning Materials, and Inks. Each section has been revised by an English expert, and where necessary alterations have been made in accordance with English practice. For comprehensiveness and reliability the book is unsurpassed, and it is too well known in analytical and college laboratories to need further recommendation.

*Food Industries*. By HERMANN T. VULTE, Ph.D., F.C.S., and SADIE B. VANDERBILT, B.S. Easton, Pa.: The Chemical Publishing Co. 1914.

This book will be useful for students of home economics who are attending a course of lectures and practical work upon the processes employed in the manufacture and preparation of foods, and the educated housekeeper who takes an intelligent interest in her work will be able to learn much from it. In order to profit by the information given in it a knowledge of physics and chemistry would be useful, but it need not be regarded as entirely indispensable. The functions and nature of different classes of food are discussed in an introductory chapter, and then each important class of food is treated in more or less detail. Much attention is paid to wheat, flour, bread, and the manufacture and uses of various cereals for breakfast foods. The packing house and the canning industry are also fully discussed, and some account is given of methods of preserving foods. The book contains much historical information, and is written in a very interesting and readable style.

## MEETINGS FOR THE WEEK.

TUESDAY, Jan. 5th. } Royal Institution, 3. (Christmas Lectures,  
THURSDAY, " 7th. } adapted to a juvenile auditory).  
SATURDAY, " 9th. } in the Home, by Prof. C. V. Boys, F.R.S.



# THE CHEMICAL NEWS.

VOL. CXI., No. 2876.

## NUMBER RELATIONS AMONGST THE ELEMENTS.

By F. H. LORING.

In studying atomic weight relations, or the classification of the elements by atomic weight, it is interesting to note that two or three types of irregularity common to one element or a series of elements, so balance or cancel each other as to leave a mean interpretation representing a normal or regular condition, or, on the other hand, the "irregularity" itself becomes regular by some symmetrical peculiarity. This principle may be tentatively illustrated by the following treatment:—

Referring to "Studies in Valency," p. 23, a periodic arrangement of all the elements is shown, which lends itself to certain uniform sub-divisions or arrangements of members which are fairly regular when interpreted in a certain manner, as will be seen from the following specification:

There appears to be a constant ratio between the number of elements comprising certain branches and the preceding number of non-branch places into which elements fit, not counting those of the chemically inactive class and nitrogen. This reckoning is from branches of the *like type*. The ratios may be expressed by placing the numbers representing the respective branch elements as denominators thus:— $21/3 = 7$ ,  $14/2 = 7$ ,  $14/2 = 7$ .

While this argument, as it stands, is opposed to the view that elements will ultimately be discovered which will take up places preceding ruthenium and osmium, that is to say, one before each, the observation in the main is true, since there is no reason to suppose that these relations are exact or precise to within, say, one unit or one element. There are, however, other relations which throw consider-

able doubt on the probability of these two elements having a real existence.

Referring again to the same table, it is further to be observed that the number of stable elements in the vertical columns containing the branches and including the branch-members themselves is equal to the number of preceding non-branch members (reckoned in the same manner) by a regular difference of 2. Here, however, a very curious condition in respect to tellurium has to be postulated, which satisfies certain other requirements, most notably the one demanding 32 elements or members in the set (6th division) terminated by tellurium.

This regularity calls for 19 elements in Group VII. of the right-hand half of the table, as if tellurium were  $Te_{17}$  (in which case  $Te_1 = 7.5$  and  $Te_{17} = 127.5$ ). The following arrangement will make this clear:—

L.....	I.	II.	III.	IV.	V.	VI.	VII.
	6	+ 5	+ 5		5	+ 5	
			2	= 18			2 = 12
R.....	I.	II.	III.	IV.	V.	VI.	VII.
	3	+ 3	+ 3	+ 3	+ 3	+ 2	
							2 = 19

In this case the non-branch elements, nitrogen, potassium, and one supposed element immediately following bismuth (Mendeleeff), are reckoned as occupying their respective chemical places in the table. An alternative apportionment of the numbers is given below, in which the hypothetical element following bismuth is assigned to Group VII., somewhat after the manner of tellurium (see table), the constant to be added being in this case 3 instead of 2, whilst nitrogen and potassium remain in their non-chemical places as shown in the table, the disposition of the numbers being:—

L.....	I.	II.	III.	IV.	V.	VI.	VII.
	5	+ 5	+ 5		4	+ 5	
			3	= 18		3	= 12
R.....	I.	II.	III.	IV.	V.	VI.	VII.
	4	+ 3	+ 3	+ 3	+ 3	+ 3	+ 1
							3 = 20

From the above it might be supposed that some balanced proportion exists between the right- and left-hand branch-members, when taking into account the radio-elements, but excluding the three chemically inactive radio-gases. Indeed, this appears to be the case since—

VII. L	VII. R	IV. L	IV. R	
7	is to	17	is to	32

The proportion, though not exact, includes the "17 little telluriums" (of course a fanciful conception, but not unlike the well-known idea of ten heliums forming argon), and implies that the radio-elements collectively form a one-branch system from lead, lead itself being a more or less composite element. There are exactly 32 distinctive radio-elements, omitting the chemically inactive radio-gases, and four probably indistinguishable end-products which would be the equivalent of lead, and counting in one undiscovered member preceding actinium (see CHEMICAL NEWS, cix., 241).

Dr. H. G. J. Moseley (*Phil. Mag.*, xxvii., 703), in recent work on the X-ray spectra of the elements, shows clearly the lacunæ for undiscovered elements, one preceding ruthenium and one preceding osmium, and confirms the inference that may be drawn from this study, that practically all the elements are known with these possible exceptions, and one in the rare-earth group between neodymium and samarium; there are also thulium I. and thulium II. which may be taken as established, or at least the X-ray spectra require also an additional element to thulium to render the progressive steps of the series of lines regular. Dr. Moseley has not as yet published an extension of his series of lines beyond gold, but there is every reason to believe that, between aluminium and gold,

\* From H to Ce (inclusive) = 52 (a).  
From Pr to Lu (inclusive) = 13 (b).  
21/3 = 7, which is the Group No. of b, just as VII. is the Group No. of the other branches, these branch Group Nos. being one unit in excess of the proper classification value, a stepping-back principle being involved in "Studies in Valency." Similarly, from Ta to Pb (inclusive) = 18, which is the Group No. of c, just as VI. is the Group No. of the other branches, these branch Group Nos. being one unit in excess of the proper classification value, a stepping-back principle being involved in "Studies in Valency." The mean valency of the chemically active radio-elements =  $(2 + 3 + 4 + 5 + 6) / 5 = 4$ . The ratio should have the same characteristic as those above and differ from this figure by one unit, but since the process of element formation in this case is probably one of devolution rather than evolution (see CHEMICAL NEWS, cix., 241), not only may the ratio be reversed, but the group number may coincide with the mean valency value, so that  $x/9 = IV$ . There appear to be 32 radio-elements proper, not counting the radio-gases. When including the end products which must form part of the branch system and be equal to four normal elements (Ac-end = 3, Ac-end = 1, Ra-end = 3, Ra-end = 1, Th-end = 3, Th-end = 1; sum = 4) the figure is increased to 36; therefore,  $36/9 = IV$ . Lead (a) is taken as an element of evolution when considered separate from the isotopic end-products of radioactive origin more or less mixed with it, or forming the entire composition = b; these may be designated thus— $Pb_a$ ;  $Pb_b$ ;  $Pb_{a+b}$ . The table given on page 23 of "Studies in Valency" calls for 64 chemically active elements in the last (7th) division, including two branches, which may be evaluated thus—1 Urr, 2 UrX, 3 Ury, 4 UrXy, 5 Urr, 6 Urr, 7 AcR, 8 AcR (actinium), 9 RadAc, 10 Ra, 11 AcR, 12 Ra, 13 Ac, 14 Ra, 15 AcB, 16 RaC, 17 AcC, 18 AcC, 19 AcC, 20 AcC, 21 AcC, 22 AcC, 23 AcC, 24 RaB, 25 RaF, 26 RaF, 27 Th, 28 MeTh, 29 MeTh, 30 RadTh, 31 ThX, 32 ThA, 33 ThB, 34 ThC, 35 ThC, 36 Th-end, 37 ThD, 38 ThD, 39 ThD, 40 ThD, 41 ThD, 42 ThD, 43 ThD, 44 ThD, 45 ThD, 46 ThD, 47 ThD, 48 ThD, 49 ThD, 50 ThD, 51 ThD, 52 ThD, 53 ThD, 54 ThD, 55 ThD, 56 ThD, 57 ThD, 58 ThD, 59 ThD, 60 ThD, 61 ThD, 62 ThD, 63 ThD, 64 ThD. The numbers are attached to the radio-elements in a manner merely convenient for counting; moreover, the order might be reversed. It will be seen that the emanations are, in a sense, interperiodic (see CHEMICAL NEWS, lxxi, ciii., 71), and when the associates part company (see CHEMICAL NEWS, cix., 241) in a homogeneous manner the separate products—or those considered as such—are, consequently, pure half-elements relative to the others, at least they may be so regarded for purposes of counting.



Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
63 × 7	64 × 6	68 × 1 <sup>c</sup>	71 × 4	72 × 3	75 × 2	79 × 1
67 × 1	68 × 3	72 × 5	73 × 7	76 × 9	80 × 11	80 × 13
63·500	65·333	71·333	72·272	75·000	79·230	79·928....Associates: m.v.
63·53	65·34	71·35	72·27 <sup>c</sup>	74·98	79·25	79·90 ....Ellip. method.
63·57	65·37	69·9	72·5	74·96	79·2	79·92 ....Experimental.
63·50	65·33	71·33				79·90 ....Summation method.
						79·90 ....Quat. series method.
Ag.	Cd.	In.	Sn.	Sb.	I.	Te.
107 × 7	111 × 7	112 × 5	116 × 5	119 × 7	126 × 1	[7·5 × (3 + 14)] = 127·5
111 × 2	115 × 4	117 × 6	121 × 8	121 × 10	127 × 12	
107·888	112·454	114·727	119·077	120·176	126·923	.....Associates: m.v.
107·9	112·47	114·72	118·99	120·16	126·96	127·5 ....Ellip. method.
107·88	112·40	114·8	119·0	120·2	126·92	127·5 ....Experimental.
107·9	112·43				126·92	.....Summation method.
107·9					126·92	127·5 ....Quat. series method.
Au.	Hg.	Tl.	Pb.	Bi.		
196 × 7	199 × 8	202 × 9		208 × 11		
200 × 3	203 × 5	207 × 7		208 × 11		
197·200	200·538	204·187		208·000....Associates: mean values.		
197·25	200·5 <sup>c</sup>	204·17 <sup>c</sup>		208·00 ....Elliptical method.		
197·2	200·6	204·0		208·0 ....Experimental.		
		204·17		.....Quaternian series method.		

## Upper atom-numbers—

7—6—1—4—3—2—1	
0...1...4...1...0...Differences.	
7—7—5—5—7—3—1*	
0...1...4...1...0...Differences.	
7—8—9—6—11—[4—1]	

\* Tellurium and Iodine in chemical place.  
c = Corrected value.

## Lower atom-numbers—

1—3—5—7—9—11—13	
2—4—6—8—10—12†—14†	
3—5—7—9—11—[13—15]	

† Iodine and tellurium in numerical place.  
[ ] = Uncertain representation relative to others.

NOTE.—The term "atom numbers" should not be confused with the *serial numbers* assigned to the elements by A. van den Broek.

all the elements are known except, at the most, four elements as above indicated. Rutherford and Andrade's (*Phil. Mag.*, xxvii., 854) experimental analysis of matter by excited radiation gives lines which assign lead to its proper and expected place in the extension of the series as indicated by X-ray analysis, and therefore no new elements are to be expected between gold and lead.\*

Upon careful consideration of these supposed elements, falling as indicated next to ruthenium, osmium, and samarium, it will be seen, however, upon referring to "Studies in Valency," p. 17, that the lacunæ for these three elements in question are of the same character in the valency plot shown, indicating possibly that these may be natural breaks in an otherwise continuous chain, since, by closing the table up at these points, the irregularity becomes in itself regular. The number relations herein given support this contention.

The table under further consideration, with respect to the right-hand half of non-radio-active elements, lends itself to a complete arrangement of associate atoms (see *CHEMICAL NEWS*, cx., 25) in suchwise as to bring into

harmony the values by the elliptical method, those of the quaternian series when available (there being a limited number of these), and those by the summation method, also limited in number. Moreover, the values are not at variance with those obtained by experiment when the more accurately determined values are compared with the theoretical ones, as the accompanying table will show. In this table, however, the atomic weights enclosed by the circumscribed line are for one reason or another uncertain, notwithstanding the coincidences. The other atomic weights for the most part are probably correct; those obtained by taking mean values (m.v.) of the associate atoms as shown being the preferred ones, and these are supported by experiment. It must be remembered that the various methods employed represent tools which are capable of *some adjustment*, and finality is not possible in every case.

The setting aside of the inactive gases in these number-studies should not be taken as an indication that they are not true elements, but rather that they are *chemically inactive*, and consequently count as nought when balancing or otherwise arranging the chemically active members. They appear to fit into the X-ray spectrum series, and take up a normal zero place in practically all periodic tables, and from various considerations the universal opinion is that they are true elements (see Soddy, *Science Progress*, 1914, viii., 654).

Since these relations are largely based upon the idea of branch systems of elements, the peculiarity of these branches should be kept in mind, otherwise some of the statements would seem contrary to accepted opinion; whereas the method of treatment is, I believe, quite as comprehensive in its systematic expression of fact as any other method, but this is a matter for others of wider experience to judge.

\* The composite nature of the atom may be revealed by some characteristic radiation—such, for example, as the X-ray spectra of the elements as experimentally developed by Moseley. As a first approximation in theory, the two characteristic lines observed might arise from the presence of two types of atoms differing in atomic weight; but theoretical considerations do not necessarily point directly to such a view. These, however, are matters which the experimenters themselves can doubtless discuss to better purpose. For a general account of the interference and reflection of X-rays by crystals and the analysis of matter thereby, see "X-Rays," by Kaye (Longmans, Green, and Co., 1914), particularly Chapter XII., but the original papers should be studied. For a list of references leading up to the developments by Moseley, see "Text-book of Inorganic Chemistry," by Messrs. Friend, Little, Turner, and Briscoe (C. Griffin and Co., Ltd., 1914), vol. i., p. 50. See also Tutton, *CHEMICAL NEWS*, 1913, cvii., 277, 289, 301; but see particularly Moseley, *Phil. Mag.*, December, 1913, p. 1024, and April, 1914, p. 703.

These relations seem to harmonise with those published in the *CHEMICAL NEWS*, 1912, cvi., 37, when main and subordinate considerations (details) are not confused. (See also *CHEMICAL NEWS*, 1913, cviii., pp. 95, 188, 247, and 305).

Greater interest than ever seems to be attached to the problem of *exact* atomic weight determination, and the following statement by Prof. Soddy (*CHEMICAL NEWS*, cviii., 169), which I am sure was not intended to minimise the importance of such work, should be of profound interest—if I may express what appears to be the opinion of others:—

"The chemical analysis of matter is thus not an ultimate one. It has appeared ultimate hitherto on account of the impossibility of distinguishing between elements which are chemically identical and non-separable unless these are in the process of change the one into the other. But in that part of the Periodic Table in which the evolution of the elements is still proceeding, each place is seen to be occupied not by one element, but on the average, for the places occupied at all, by no less than four, the atomic weights of which vary over as much as eight units. It is impossible to believe that the same may not be true for the rest of the table, and that each known element may be a group of non-separable elements occupying the same place, the atomic weight not being a real constant, but a mean value, of much less fundamental interest than has been hitherto supposed. Although these advances show that matter is even more complex than chemical analysis alone has been able to reveal, they indicate at the same time that the problem of atomic constitution may be more simple than has been supposed from the lack of simple numerical relations between the atomic weights."

Whatever else these relations may signify, they certainly broaden one's conception of Nature's working, in that the observing student must no longer look at things through one pair of spectacles but through several of different character or colour before the composite design is fully brought to view.

## THE INTERSTRAIN THEORY OF HARDNESS.\*

By ANDREW McCANCE.

1. THERE are three methods by which a pure metal may be made harder, namely, by mechanical deformation, by the addition of elements which form solid solutions, and by the application of heat treatment (in certain cases), but as yet there is no theory which can be said to demonstrate the underlying connection which must exist between these three means of achieving the same end. For it can be said with certainty that so long as the metal retains its chemical characteristics the same effects must be derived from the same immediate causes.

It is with the hardening effect caused by heat treatment that this short paper will deal, but it can be shown that what is true for iron is also generally true for all alloys where corresponding conditions exist.

2. The great amount of attention which has of late been concentrated on the nature of the allotropic changes in pure iron has made it clear that from ordinary temperatures up to 1000° C. only two real allotropic forms of iron exist, the  $\alpha$  and the  $\gamma$ , and that the so-called  $\beta$  iron is in reality  $\alpha$  iron which has become non-magnetic from purely thermal causes, the apparent liberation of heat at  $A_2$  being due to the rapid change in the specific heat which necessarily accompanies the ferromagnetic transition (McCance, *Four. Iron and Steel Inst.*, 1914, i., 223; Benedicks, *Ibid.*, 1914, i., 439).

Since  $\alpha$  iron loses its magnetic properties above a definite temperature, it might be suggested that  $\gamma$  iron, which

at high temperatures is non-magnetic, might itself become magnetic at lower temperatures. Non-magnetic manganese steel, however, is not transformed even at the temperature of liquid air (Hadfield, *Four. Iron and Steel Inst.*, 1905, i., 179), and no treatment can make austenitic steels magnetic which does not increase the specific volume at the same time, and when this takes place it points conclusively to the transformation to  $\alpha$  iron, for the thermal magnetic transition makes no appreciable alteration in the specific volume.

The development of enormous crystals in low carbon steels which have been strained and afterwards reheated to any temperature below  $A_3$  (Stead, *Four. Iron and Steel Inst.*, 1898, i., 145; Chappell, *Four. Iron and Steel Inst.*, 1914, i., 472), and in thin sheets of electrolytic iron cooled from above  $A_3$  (Stead and Carpenter, *Four. Iron and Steel Inst.*, 1913, ii., 113), proves that iron possesses the same crystalline form above  $A_2$  as below it, and that therefore the  $A_2$  point is not evidence of allotropy.

3. The great and important distinction between the two forms of iron is their behaviour towards carbon, which is soluble in  $\alpha$  iron only to a very small extent, but can dissolve with readiness in  $\gamma$  iron, and on this preferential treatment rests the explanation of the unique position which carbon occupies as a cause of hardening by quenching in iron. There is no doubt that if another element can be found which possesses the same property of exclusive solubility in  $\gamma$  iron, then that element also will possess to a similar extent the hardening power of carbon.

4. Pure iron, in common with all metals, is hardened after permanent deformation, and it is best described after such treatment as being in a condition of "interstrain." Metals in their normal unstrained condition are crystalline. That is, they are composed of an orderly arrangement of their constituent atoms arranged in a space lattice which conforms with whatever symmetry the crystals possess. Successful attempts have been recently made by the aid of X-rays to determine the actual position occupied by the atoms, and copper (Bragg, *Phil. Mag.*, September, 1914), for instance, has been shown to have its atoms built up in a "face centred" cube—that is, a cube having an atom at each corner and one at the centre of each face.

The effect of deformation on such systems must be to alter the position of each atom relatively to its neighbour, and permanent deformation must cause so much alteration that the atoms along the planes of slip can no longer return to their positions of equilibrium. This corresponds to the condition of interstrain, and results in a hardening of the material. That the destruction of the crystalline arrangement goes so far as to render the material in those planes of greatest movement actually amorphous and devoid of crystalline form, as Beilby has proposed, has never been seriously questioned, but the writer thinks that the following facts are strong arguments against this theory of a hard, vitreous, amorphous phase. In the case of a dimorphous metal like iron, the vitreous phase to be truly amorphous must possess the same physical properties, no matter from which crystalline form it has been produced by deformation, and since strained  $\alpha$  iron loses none of its magnetic intensity, we must assume that amorphous iron is magnetic; consequently it is to be expected that strained  $\gamma$  iron will also be magnetic since the same constituent is produced. The important results of Hadfield and Hopkinson (*Four. Iron and Steel Inst.*, 1914, i., 125) show, however, that the magnetic intensity of austenitic manganese steel after severe straining is only augmented to 0.3 per cent of the intensity of pure iron, and is still practically non-magnetic, although the hardness has increased from 200 to 490. It would seem that the iron in the interstrained condition has not lost the distinguishing properties which are the result of crystalline form.

Hanriot (*Comptes Rendus*, clv., 713, 1502) exposed small cubes of metal to a fluid pressure of 10,000 kgs. per sq. cm., and although no measurable deformation could be detected, the hardness had increased in every case as follows:—

\* Contribution to the General Discussion on "The Hardening of Metals," held before the Faraday Society, November 23, 1914.

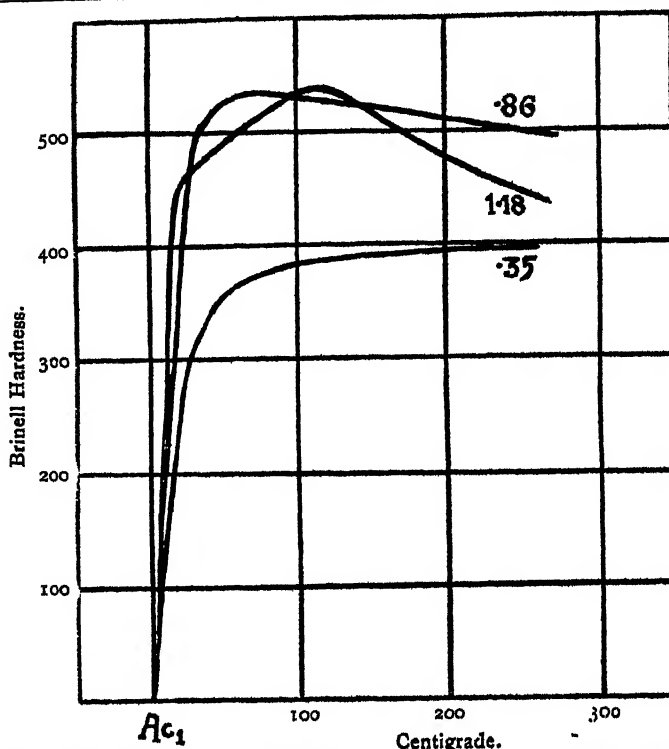


FIG. 1.—The units are degrees Centigrade above the  $Ac_1$  point, and increase in hardness in Brinell numbers above the annealed value.

Metal.	Hardness (before).	Hardness (after).
Silver	20.3	32.2
Iron	57.7	62.3
Brass	24.0	36.5
Zinc	33.1	43.0

The microstructure was the same after this treatment as before, while to suggest that the hard vitreous phase had been formed as the result of pressure would, of course, be out of the question, since iron which expands on becoming liquid would have its melting-point raised and not lowered by pressure.

Deformation does not necessarily produce an amorphous constituent, but only results in some permanent alteration of the atoms from their positions of equilibrium in their crystalline space lattice; and, conversely, it will be true that any metal whose atoms are prevented from reaching their positions of equilibrium will be in a condition of interstrain, and will be hardened.

5. To harden steel it is necessary to heat it above the  $Ac_1$  point—that is, to heat it to the temperature at which the carbon is all in solution, and then to cool it at a rate which is sufficiently rapid, but the greatest hardness is obtained when the temperature reaches the highest change point—that is the  $Ac_3$  for hypoeutectoid and  $Ac$  cementite for hyper-eutectoid steels. This is shown in Fig. 1, giving the hardness of three steels with 0.35 per cent, 0.86 per cent, and 1.18 per cent carbon, and the temperature of quenching in degrees above the  $Ac_1$ .

With 0.35 per cent carbon the structure, after quenching from just above the  $Ac_1$  will consist of ferrite and martensite areas (separated by transitional troostite, &c.), and the increase in hardness from this to just above the  $Ac_3$ , when the structure is wholly martensitic, corresponds with the gradual replacement of the ferrite by the hardest constituent. With 1.18 per cent carbon the greatest hardness is obtained by quenching from just above the  $Ac$  cemen-

tite, and the softening which takes place on increasing the temperature corresponds with the appearance of austenite in the microsection. A very important result is that when the carbon reaches about 0.7 per cent a maximum hardness is obtained in the quenched state, and this value is not exceeded in any pure carbon steel. If the hardness were the direct consequence of carbon in solution, the hardness would be proportional to the amount of carbon dissolved. That it is not so shows that the action of carbon is indirect, and that the hardening element is the iron itself.

6. It is a fact well known that steels which at the temperature of quenching are non-magnetic are magnetic in their hardened state, and this change must have taken place during the time occupied by the quenching. Since it has been previously shown that  $\gamma$  iron does not itself become magnetic, it is necessary to conclude that during the time occupied in cooling from the higher temperature to the lower the original  $\gamma$  must have changed to the magnetic  $\alpha$  condition. Measurements of the electric resistance show that the carbon has not changed its condition, but has remained in solution, and so we recognise the fact that under the conditions of quenching the transformation of the iron from the  $\gamma$  to the  $\alpha$  state can take place independently of the change in the state of the carbon from a state of solution to the undissolved state. These two transformations, which on slow heating and cooling take place simultaneously, can behave as independent reactions, although in a sense which is limited. For though martensite may be considered as an enforced solution of carbon in  $\alpha$  iron, it must not be forgotten that there is still some  $\gamma$  iron present with the carbon, which is absolutely necessary to maintain its solubility, and any change in the state of the carbon causes the transformation of this  $\gamma$  iron to  $\alpha$ . It might on this account be suggested that the iron is chemically combined with the carbon, but an examination of the curve (Fig. 2) connecting the loss of

magnetic saturation intensity with the carbon content shows that the  $\gamma$  iron increases much more rapidly than the amount of carbon, which points to purely physical influences.

7. It has been shown elsewhere (McCance, *loc. cit.*) that it is possible to calculate the velocity of quenching in a round bar on certain assumptions which are closely realised in the early stages, at least of quenching, and if the curve thus obtained is compared with the curve connecting the electric resistance, or the loss of magnetic intensity of a steel with 0.86 per cent carbon, it is seen that they are closely similar, so that the amount of carbon in solution and the amount of  $\gamma$  iron retained in the cold state are proportional to the rate of cooling, at least until the carbon is completely in solution.

With a given rate of cooling the progress of the transition from the equilibrium position for  $\gamma$ -crystals to that

The first of these can take place independently of the second, but when the second takes place it necessarily involves the first. Three possible conditions can therefore result:—

- (1) Both transformations are completed: this is the normal pearlitic condition of steel, which is soft.
- (2) Both transformations are suppressed; this corresponds to the condition of pure austenite, which is also comparatively soft.
- (3) When (a) takes place but (b) is suppressed—that is, the complete transformation is partially suppressed—then the structure is martensitic and the  $\alpha$ -iron formed under this condition is interstrained and very hard.

Case (3), then, is the important one from a hardening standpoint, and to be possible it is necessary that a difference should exist in the respective velocities of transformation of (a) and (b), so that with an appropriate rate of cooling the slower transformation can be suppressed while the faster is not greatly affected.

This intimate connection between the rate of cooling and hardening is further illustrated by the behaviour of alloy steels. The addition of manganese, for instance, by lowering the temperature of the transformations greatly decreases the velocities with which they proceed, so that with a certain percentage (which varies with the carbon content) the transformation of the carbon may be almost completely suppressed by air cooling, and the normal condition after such treatment is martensitic, accompanied by hardness and brittleness—in fact, all the characteristics of quenched pure carbon steels. Water quenching, on the other hand, results in the complete suppression of both transformations, and the steel becomes austenitic and soft, while the same result is obtained by air cooling when the percentage of manganese is further increased.

Commercial manganese steels after air cooling are non-magnetic though fairly hard and brittle, but such steels usually contain about 1.2 per cent of carbon, and this condition is probably brought about by the deposition from a state of solution of the cementite in excess of the eutectoid composition.

Similar results are obtained by the addition of nickel, and the following facts are also instructive. A nickel steel containing 3.6 per cent of Ni and 0.19 per cent carbon had a normal hardness of 183, which, after quenching in water from 1000° C., had risen to 444; but a steel containing 0.19 per cent carbon without the nickel increased after the same treatment from 143 to 218; that is, while the plain carbon steel increased in hardness 65 points by quenching, the nickel steel increased by 259. Nickel is known not to form a carbide in this range of composition (Arnold and Read, *Engineering*, 1914, pp. 463 and 468), consequently the state of the carbon is similar in both, and the increased hardening power must be due to the influence of the nickel on the iron. It has enabled the iron to retain a greater degree of interstrain by lowering the temperature at which the transformation of the  $\gamma$  to  $\alpha$  iron takes place.

8. Tempering allows the metastable conditions which result from quenching to revert to their stable state. In hypoeutectoid steels the carbon is deposited from solution and the specific resistance falls, while at the same time the interstrained condition of the iron is gradually lost with the formation of a ferrite recognisable under the microscope (McCance, *Four. Mechan. Eng.*, 1910, p. 1664). As a consequence, the magnetic permeability under low fields increases, the remanent magnetism decreases, and the peculiar shape of the curves connecting the magnetic properties with the temperature of tempering is found to be exactly similar for interstrained iron as for quenched steels—a similarity which extends also to the rate at which the hardness is lost (Maurer, *Rev. de Mit.*, 1908, p. 711).

Turning now to the consideration of the tempering of high carbon steels which contain a proportion of pure austenite, the curves of specific volume electric resistance

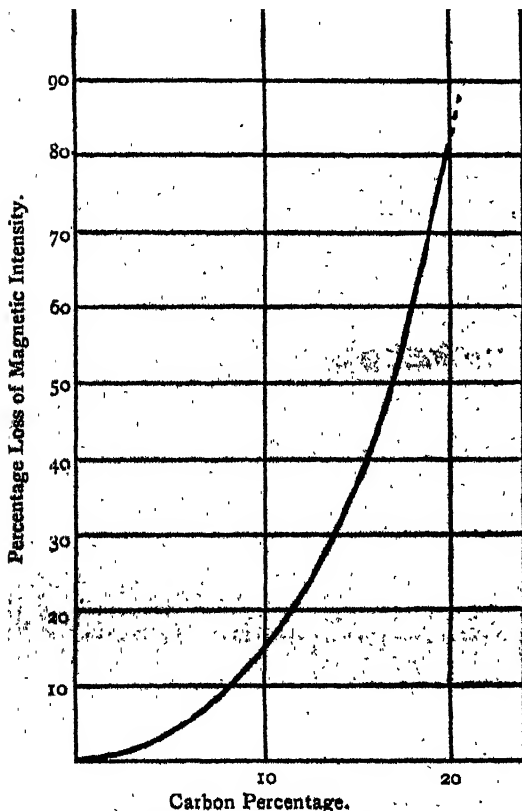


Fig. 2.—From data published by Hadfield and Hopkinson and by the Author.

of  $\alpha$ -crystals will be arrested, and will ultimately be stopped by the increase in the internal viscosity at the lower temperature. The crystalline transformation, in other words, will be partially suppressed, and a condition produced which is essentially similar to the condition of interstrain produced by deformation, and the hardness which results is accounted for by this condition.

During the cooling of hypoeutectoid steel from a temperature at which it consists of a homogeneous solution of carbon in  $\gamma$ -iron, its complete transformation into  $\alpha$ -iron and cementite comprises two individual transformations:—

- (a) A change in the state of the iron from  $\gamma$  to  $\alpha$ .
- (b) A change in the state of the carbon.

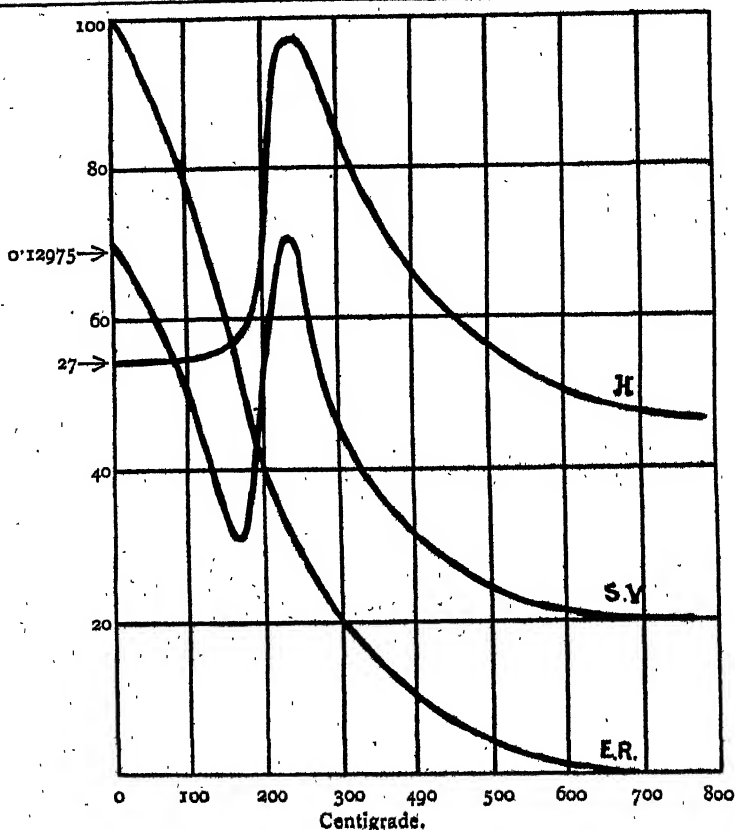


FIG. 3.

H. = Hardness curve—each vertical division represents 10 units (Shore).  
 E.R. = Electric Resistance—each vertical division represents 20 per cent of the total loss.  
 S.V. = Specific Volume—each vertical division represents 0.0004 cub. cm.

and hardness of one containing 1.66 per cent carbon due to Maurer are given in Fig. 3.

The smooth curve for the electric resistance shows that the carbon is deposited continuously, and this causes a decrease in the specific volume, but at 150° C. to 250° C. there is a sudden increase which is without effect on the electric resistance, and must, therefore, be due to the transformation of  $\gamma$  to  $\alpha$  iron, and since this takes place independently at a low temperature under conditions of high internal viscosity, the  $\alpha$ -iron formed will be in a condition of interstrain, and an increase in hardness should result. This is strikingly confirmed.

9. The importance of internal friction in retarding transformations and preserving the metastable state has been pointed out, and in solids this internal friction is very similar to sliding friction between solid surfaces. A fixed amount of super-cooling below the transition range, for instance, is necessary before transformation can take place in solids, and the difference in the temperature of transformation on heating and cooling is a measure of the internal friction. Twenty-five per cent nickel steel has a transformation-point at 550° C. on heating, while on cooling it is transformed in the neighbourhood of -100° C., which shows a range of 650°; but manganese steel containing about 14 per cent Mn has a larger difference in this respect than any other, since on heating the Ac point occurs about 550° C., while the Ar<sub>1</sub> does not even take place at the temperature of liquid air, a range of more than 740°.

Many of the abnormal properties which manganese steel possesses are due to this great friction. Deformation

renders non-magnetic nickel steel magnetic through the transformation of the  $\gamma$ -iron to  $\alpha$  with a decrease in density, but manganese steel, on the other hand, is practically unaffected magnetically.

Tempering at a temperature just below its change-point results in the gradual conversion of the  $\gamma$ -iron to  $\alpha$ , and the deposition of the carbon from solution, but the  $\alpha$ -iron is interstrained and the hardness is increased. It is conceivable that very prolonged tempering would cause this hardness to be lost again, with the production of a soft manganese steel which is magnetic.

10. When pure austenite, formed by quenching 2 per cent manganese steels, or the austenite of high carbon steels, is immersed in liquid air, the greater super-cooling overcomes the internal friction, and the  $\gamma$  to  $\alpha$  transformation takes place, although the carbon change is unaffected. The electric resistance is not changed, but the specific volume increases as well as the hardness, through the production of interstrained  $\alpha$ -iron. Maurer obtained the following results:—

Composition. Per cent.	Electric Resistance.	Specific Volume.	Hardness.	Magnetic Remanent. cm.
1.66 C.	1.00	0.12964	28	14.5 (a)
1.66 C.	1.04	0.13105	38	28.5 (b)
1.94 C.	1.00	0.13233	17	0.8 (c)
2.24 Mn.	1.07	0.13439	29	8.2 (d)

(a) Quenched from 1100° C. in iced brine.

(b) Quenched from 1100° C. immersed in liquid air.

(c) Quenched from 1200° C. in iced brine.

(d) Quenched from 1200° C. immersed in liquid air.

11. The theory outlined above accounts for the many widely differing conditions which steel can assume as the result of heat treatment, in a manner which is simple and consistent.

It is agreed that hardening by deformation results from purely structural causes which affect the crystalline state, and there is much to recommend the term "interstrain" to describe such a condition of hardness, since it is a word which is non-committal regarding any proposed explanation of the effect. The theory of inter-strain action is itself an inquiry, but it is secondary to the main issue in the hardening of steel.

# THE RATE OF LIBERATION OF HYDROCYANIC ACID FROM COMMERCIAL KINDS OF LINSEED.

By S. H. COLLINS, M.Sc., and H. BLAIR.

WHEN linseed is crushed and moistened, hydrocyanic acid is slowly formed by the action of an enzyme on a cyanogenetic glucoside. The amount of hydrocyanic acid and the rate at which it is given off both depend on a variety of conditions. Both amount and rate have a bearing on the safety of linseed as a cattle food. (See "The Rate of Evolution of Hydrocyanic Acid from Linseed under Digestive Conditions," *Univ. Durham Phil. Soc.*, iv., 99, and "The Rate of Liberation of Hydrocyanic Acid from Linseed," *Analyst*, 1914, p. 70).

The object of the present communication is to show some of the variations in the amount and rate of evolution of hydrocyanic acid due to variations in the place of origin of the seed. Under the Essex County Council there have been carried out several experiments to test the practical value of linseeds of different origin. Owing to the kindness of Mr. E. M. Taylor, the Chemist to the East Anglian Institute of Agriculture, we have been able to determine the amounts of hydrocyanic acid in many of the seeds grown under experimental conditions. These linseeds yielded in Essex from 10 to 18 cwt. seed per acre, and 10 to 34 cwt. straw per acre. The seeds contained from 30 to 39 per cent oil and 20 to 23 per cent albumenoids.

Table I. gives the names of the districts from which the seed originated. In all cases the seed was sown and reaped in Essex, and the seeds actually tested were the first year's home-grown seeds from crops grown with foreign seed. The column showing the total amount of hydrocyanic acid gives the amounts liberated under the conditions described in *Univ. Durham Phil. Soc.*, iv., 99, during a period of five hours at 45° C.

The column showing the rate of liberation gives the number of minutes necessary to liberate one-half of the total amount of hydrocyanic acid. The figures in this column vary inversely with the enzymic activity. The enzymic activity may vary with the amount of enzyme present, but other causes will also act.

The criterion of safety for cattle feeding will be a small figure in the first column and a large figure in the second column.

A study of Table I. shows that there is great variation in both amount and rate. The seeds of Oriental origin, Calcutta, Bombay, and Japan are all high in total hydrocyanic acid and rich in enzymic activity. On the other hand, the seed derived from Morocco is low both in hydrocyanic acid and in enzymic activity. These results are exactly in agreement with those obtained in former years by testing seed direct from foreign countries, and may therefore be regarded as permanent characteristics of the districts concerned.

Table II. gives the results obtained from seed grown in foreign places as stated, together with some samples of seed grown in the College garden, which had been grown there for many years, but had originally come from India. These results are still further compared in Table III.,

which shows the results of growing foreign seed in England. It will be seen that the general result of growing linseed in England is to reduce the total amount of hydrocyanic acid and to increase the activity of the enzyme. These results are in conformity with some previous results obtained by growing linseed in pots in the greenhouse, some being grown with the minimum and some with the maximum amount of water that was compatible with a fair crop. In these cases the linseed grown with the minimum amount of water contained more hydrocyanic acid and showed a slower rate of evolution than did the linseed grown with the maximum amount of water. Similarly, linseed grown in the garden in the dry summer of 1911 showed more hydrocyanic acid and a lower rate than did the linseed grown in the wet summer of 1910.

TABLE I.—*First English Crop from Foreign Seed.*

Origin of seed.	Hydrocyanic acid. Parts per 1000.	Minutes to evolve one-half total amount.
2 Memel, North Russia ..	0.088	70
0 Reval, North-Russia ..	0.197	60
15 Libau, North Russia ..	0.195	28
19 Windau .. .. .	0.175	35
15 Steppe, Russia .. .	0.160	35
1 Mancupel, South Russia ..	0.170	55
4 Theodosia, South Russia ..	0.123	75
3 Berdiansk, South Russia ..	0.105	90
14 Nicolaieff, South Russia ..	0.105	90
16 Eupatoria, South Russia ..	0.173	35
10 Ghenitchesk, South Russia	0.175	35
21 Koenigsberg, Germany ..	0.213	55
7 Kustendji, Roumania ..	0.183	45
8 Bralla, Roumania .. .	0.115	55
13 Turkey .. .. .	0.108	75
9 Morocco .. .. .	0.112	60
6 Bombay .. .. .	0.210	35
8 Calcutta .. .. .	0.233	40
12 Japan .. .. .	0.270	55
Average .. .. .	0.164	56

TABLE II.—*Linseed from various Sources.*

Locality.	Hydrocyanic acid. Parts per 1000.	Minutes to evolve one-half total amount.
College garden, minimum ..	0.126	45
College garden, maximum ..	0.170	90
Irish .. .. .	0.275	85
Riga .. .. .	0.225	65
Morocco .. .. .	0.151	55
Bombay, minimum .. .	0.260	45
Bombay, maximum .. .	0.300	62
Calcutta, minimum .. .	0.250	46
Calcutta, maximum .. .	0.380	50
Plate .. .. .	0.175	70
Average .. .. .	0.231	61

TABLE III.—*Effect of Home Growth on Foreign Linseed.*

Bombay, foreign grown ..	0.280	54
Bombay, once home grown ..	0.210	35
Calcutta, foreign grown ..	0.315	48
Calcutta, once home grown ..	0.233	40
Morocco, foreign grown ..	0.151	55
Morocco, once home grown ..	0.112	60
Riga, foreign grown .. .	0.225	65
Riga, twice home grown ..	0.165	35

By collecting all the information under this head and arranging as far as possible a contrast between those linseeds grown under conditions of drought and heat with those grown under conditions of damp and cold, the following results are obtained.

The average result of changing seed from dry and hot conditions to damp and cool conditions is to depress the



hydrocyanic acid evolved by  $20 \pm 3$  per cent and to reduce the half time rate by  $24 \pm 5$  per cent.

There is no doubt that these commercial varieties of linseed are mixed and genetically impure. I am, however, in hope that I may be able to obtain some genetically pure seed and continue these investigations. Meanwhile it would seem that English grown seed is safer than foreign grown seed for the purposes of cattle food, but that before further experiments on the growth of linseed are carried out in England, it would be well to see that the seed selected for such experiment was of a variety likely to give a linseed low both in cyanogenetic glucosides and enzymes. There is not much correlation between yield of seed per acre and cyanogen content, but on the whole there is a tendency for the seeds having an origin in temperate climates to give the best yield per acre and to contain the least proportions of cyanogenetic glucosides.—*Proceedings of the Durham Philosophical Society*, v., Part 4.

### BRITISH DYES.

At a meeting of representatives of important firms and associations making use of artificial dyes, held at the Board of Trade on Tuesday, November 10, 1914, the following resolution was unanimously passed, namely:—

"That this meeting approves in principle of a national effort being made by the trade to increase the British supply of synthetic colours, and welcomes the assistance of His Majesty's Government for that purpose, and that the following gentlemen be and are hereby appointed a Committee as representing the trades concerned, with authority to confer with the representatives of the Board of Trade with a view to the elaboration of a scheme on the lines of the memorandum submitted."

The Committee appointed was:—

Mr. Lennox Lee (Calico Printers' Association, Ltd.).  
Mr. Milton S. Sharp (Bradford Dyers' Association, Ltd.).  
Mr. H. W. Christie (United Turkey Red Co., Ltd.).  
Mr. Chas. Diamond (English Sewing Cotton Co., Ltd.).  
Mr. G. Marchetti (John Crossley and Sons, Ltd.).  
Mr. R. D. Pullar (J. Pullar and Sons, Ltd.).

This Committee has been engaged upon the elaboration of the scheme referred to in the resolution, which involves the formation of a joint stock company, having for its object the manufacture and supply of synthetic colours.

The outbreak of the present War has demonstrated the dangers which surround British trade through dependence upon Germany for supplies of dye stuffs. The gravity of the situation is shown by the following extract from a speech made by Lord Moulton in the Town Hall, Manchester, on Tuesday, December 8, 1914.

Lord Moulton said:—"When I began to investigate the question of the lack of dyes I found England consuming £2,000,000 worth of dyes a year. Those dyes were essential to an industry of something like £200,000,000 a year, on which at least 1,500,000 workmen were dependent. Of that £2,000,000 worth of dyes barely one-tenth was produced in this country."

Lord Moulton pointed out that this gravity would not under the present circumstances be lessened by the return of peace. The British textile and other industries would still be left at the mercy of their present foes, as they would be dependent on a supply of dyes from them, and our experience of German methods of trade was sufficient to convince us that such supply would only be given on terms which would be most unfavourable to the competition of our industries with those of Germany. The only efficient remedy was the establishment of a company which would be capable of supplying substantially the needs of British industries for dyes. Owing to the long

period during which German chemical industries have been allowed to develop without challenge from us, Lord Moulton expressed his belief that such an undertaking must be the result of a great national effort, in which the Government took part. Success would depend on its possessing the three characteristics of being—(1) large, (2) British, and (3) co-operative.

His Majesty's Government are prepared to assist such an effort on the following lines:—

(a) A limited company to be formed under the Companies Acts, with a share capital of £3,000,000, divided into 3,000,000 shares of £1 each. This capital to be subscribed by those interested, and be paid up as to 2s. 6d. a share on allotment, ss. on June 30, 1915. The remaining 12s. 6d. is not likely to be needed for some time to come, and when required will only be payable in calls not exceeding 2s. 6d. a share, at intervals of not less than six months between each call.

(b) The Government to advance to such company £1,500,000, bearing interest at the rate of 4 per cent per annum, and secured as a first charge on the assets and undertaking of the company, and be repayable in 25 years.

(c) The interest on the advance and a Sinking Fund for its repayment are to be payable only out of the net profits of the company, but are to be cumulative.

(d) The Government advance to be made as to £750,000 on the Government being satisfied that the £3,000,000 capital of the company has been fully subscribed, and the remaining £750,000 so soon as the call of ss. a share has been made.

(e) The Government shall have the right of appointing two directors of the company, with power to veto any undue encroachment on the businesses of British manufacturers of products other than dyes and colours, or the giving of any undue preference as regards supply, prices, or otherwise to consumers of the company's products.

(The names of the gentlemen so appointed are Sir Gilbert H. Cloughton, Bart., Chairman of the London and North-Western Railway Company, and Sir Frank Forbes Adam, C.I.E.)

(f) The company shall remain British.

The opinion expressed by Lord Moulton is strongly held by the Committee, who consider that the condition of co-operation would be best secured by the subscription of the company's share capital by those interested, and also by a contract being entered into between the company and the consumers or users of its products, whereby the consumers should agree for a period of five years after peace is established, or five years after the expiry of existing contracts and of all deliveries thereunder (whichever is the longer period), to take their supplies from the company, in all cases where the company is able to supply the same of good quality and at reasonable prices, but with a provision that if a consumer should consider the prices fixed by the directors of the company too high he may require that the prices to be charged shall be determined by an independent referee.

To meet the difficulties of the present situation, it is proposed to take over certain existing colour works, and use the plants to their full capacity for the manufacture of such dyes as are essential.

Negotiations with Read, Holliday, and Sons, Ltd., have resulted in arrangements being made for the extension of their plant, so as to secure a material increase in their output, and it is proposed that the new company shall take over the business and undertaking of Read, Holliday, and Sons, Ltd., under an option which has been obtained.

It is intended to negotiate for the acquisition of other businesses which it may be desirable to take over and extend in the same way as that of Read, Holliday, and Sons, Ltd., and also to take steps to acquire a suitable site and erect and equip works thereon.

This effort to create a great national industry does not

preclude arrangements being made on co-operative lines with existing concerns in Switzerland, and the Committee have grounds for hoping that such arrangements will be possible.

Although the immediate supply of dyes must be inadequate in some respects, the Committee have reason to believe that the company will be in a position to make arrangements which will protect the country from the consequences of a famine in respect of a large proportion of the dyes essential to the textile and other industries, and ultimately to secure those industries from any repetition of that foreign domination which is the cause of their present difficulties.

With the object of securing for the company impartial administration of its business as between the users of dyes it is intended that the Board of the company (other than the Government directors) shall be selected by the Committee, and mainly composed of business men who are not themselves necessarily engaged in the dyeing trade. The Board will be assisted by an Advisory Committee, constituted from among the representatives of the users of dyes, and will, in addition, have the advantage of the advice of chemical and other experts.

In the course of their deliberations the Committee have had addressed to them, among other questions, inquiries as to whether the company would not be hampered (1) by inability to secure the requisite alcohol free of duty and (2) by restrictions at the instance of German holders of British patents. The Committee have satisfied themselves with regard to (1) that the company will be able to obtain from the Board of Customs and Excise permission to use alcohol for all industrial purposes, free from duty, by arranging that the denaturing of such alcohol shall be carried out under conditions which will not hamper its use for such purposes; and with regard to (2) that the new Act of 1914 and the rules thereunder will enable the company to obtain on reasonable terms a licence from the Board of Trade for the duration of the patents empowering it to manufacture commodities covered by such patents, so as to enable the community to enjoy the full use of the patented invention.

The offices of the Committee are at 7, Norfolk Street, Manchester.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, December 3, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, and, subsequently, Dr. M. O. FORSTER, F.R.S., in the Chair.

THE PRESIDENT announced, with deep regret, that Dr. Cecil Reginald Crymble, of University College, London, who was elected a Fellow on May 4, 1911, had been killed in action on November 20.

Mr. J. de Carle Smith was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Sidney Albert Brazier, M.Sc., 2, Mansfield Villas, Yardley Wood Road, Moseley, Birmingham; Neal Brodie, B.Sc., Government Test House, Alipore, India; John Gerald Frederick Druce, Coombe End, Whitechurch, Reading; Charles Hinde, 936, 8th Avenue West, Vancouver, British Columbia; Ronald MacInnes, 17, Shrewsbury Road, New Southgate, N.; Arthur Dawes Robinson, B.A., Bradley Court, Mitcheldean, Glos.; Ramtaran Sen, L.M.S., Bacteriological and Chemical Laboratory, Shillong, Assam, India; John Taylor, M.Sc., 3, Laurel Villas, Mardyke, Cork; Henry Terrey, B.Sc., University College, Gower Street, W.C.; Su-Hian Ting, 136, Latchmere Road, Clapham Common, S.W.

Messrs. J. A. Goodson and H. King were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Hugh Logie Allan; Henry Atlas; William Bacon, B.Sc.; Charles Kelway Bamber; Srish Chandra Banerji; Durgasanker Bhattacharje; Arthur Henry Bowell; Alexander John Boyd; John Bradshaw, M.Sc.; Frank Brinsley, M.Sc.; James Meikle Brown, B.Sc.; John Arthur Cresswick; Harry Cunliffe; Frederick Raine, Ennos, B.A., B.Sc.; James Ferguson; Alexander Fleck, B.Sc.; Ernest George, B.A.; George Noel Grinling; Thomas Clifton Hurford; Charles Cochrane Iles, M.D., D.P.H.; George von Kaufmann, jun.; George King, M.Sc.; Herbert Levinstein, M.Sc., Ph.D.; Joseph Frederick Levy; James Lyttle McKee, B.A., Ph.D.; Benjamin Stanley Mellor, M.Sc.; Alfred Edgar Newland; Henry Cecil Ratcliffe; Joseph Drummond Robertson; Rajkumar Sen, M.Sc.; William Kershaw Slater, B.Sc.; Henry Michael Spiers, B.A., B.Sc.; Alan West Stewart, D.Sc.; Mark Thompson; Olin Freeman Tower, Ph.D.; Hugh Vivian; Arthur Henry Wardle.

Of the following papers those marked \* were read:—

\*287. "A Redetermination of the Atomic Weight of Tin." By HENRY VINCENT AIRD BRISCOE.

The atomic weight of tin has been redetermined by measurement of the ratio  $\lambda_{Ag} : SnCl_4$ .

The stannic chloride was prepared from pure commercial tin and pure chlorine, and was purified by repeated fractional distillation. Its final purification and collection in weighed bulbs was effected by its decantation and fractional distillation in a sealed and exhausted apparatus.

The amount of silver required to react with the chloride present was ascertained by a gravi-volumetric method, the end point being found by nephelometric tests. Precipitation of metastannic acid produced by the hydrolysis of stannic chloride in dilute solution during the analyses was prevented by the addition of oxalic acid or tartaric acid. All the usual precautions were taken.

Fifteen concordant analyses of fifteen separate fractions of stannic chloride give for the atomic weight of tin a mean value approximating closely to 118.70.

### DISCUSSION.

Dr. SCOTT remarked that previous determinations of the atomic weight of tin seemed to centre round one or other of the numbers 118 and 119. The earlier experiments pointed to the lower number, whilst the later very concordant results of Bongartz and Classen (who employed five different ratios) seemed to indicate the higher number as the true value. A thorough revision on modern lines was therefore urgently needed, and he was glad the author had undertaken this work, even although that had resulted in a value between the two whole numbers given, thus removing tin from the list of elements the atomic weight of which closely approximated to a whole number.

The obvious method of determining the atomic weight of an element by converting it into an oxide, or a lower oxide into a higher one (or the reverse process), too often gave unsatisfactory results, especially when the element formed a series of oxides. This suggested that perhaps a series of chlorides might be no better, and the higher chloride might be the most unsuitable when the behaviour of the higher chlorides of mercury, antimony, and phosphorus on vaporisation was recalled. The author depended almost entirely on fractional distillation for the purification of his stannic chloride. Dr. Scott agreed with the author that the methods, as well as some of the substances, employed by Bongartz and Classen were almost certain to give too high results.

In reply to the President, Mr. BRISCOE stated that it was not to be supposed that liquid chlorine supplied in steel cylinders was entirely free from impurity, but that such impurity, if present, would be eliminated during the subsequent fractionation of the stannic chloride; in any



case, the purity of the chlorine was probably of the same order as that of the tin.

Replying to Dr. Scott, the author said that the difficulties attending the fractionation in a vacuum were such that the investigation of the original end-fractions, in which the impurities might have been expected to accumulate, was not undertaken.

The possibility that stannic chloride might dissociate into stannous chloride and chlorine had not been overlooked, but considering that the distillations took place below 30°, and that the chloride was, in most cases, condensed at the temperature of liquid air, it seemed likely that no dissociation occurred, or that if it did occur, the chlorine would be eliminated in the early fractions.

With reference to Dr. Senter's criticism that only one substance, stannic chloride, was analysed, it was pointed out that tin formed so few compounds suitable for precise manipulation or analysis that the choice of ratios was very limited.

\*288. "The Isomerism of the Oximes. Part. VI. p-Dimethylaminobenzaldoxime." By OSCAR LISLE BRADY and FREDERICK PERCY DUNN.

Contrary to expectation it has been found that p-dimethylaminobenzaldoxime exists only in the *anti*-form, all attempts to prepare its isomeride having failed. The diphenylcarbamyl derivative, however, like the diphenylcarbamyl derivatives of other aromatic aldoximes, has the *syn*-configuration; on the other hand, it is possible to obtain two carbanilino-derivatives, one of *anti*- and the other of *syn*-structure.

#### DISCUSSION.

In reply to Dr. Forster, Mr. BRADY said that the question of inner-salt formation had been considered, but the authors were of opinion that this would not take place in the presence of the excess of hydrogen chloride in the formation of the hydrochloride. The possibility of salt-formation at the dimethylamino- in preference to the oximino-group seemed to be unlikely in view of the fact that an identical hydrochloride was obtained by the action of the oxime with hydrogen chloride and by heating the aldehyde to 50° in alcoholic solution with hydroxylamine hydrochloride.

\*289. "Organo-derivatives of Bismuth. Part II. The Stability of Derivatives of Quinquevalent Bismuth." By FREDERICK CHALLENGER and CHARLES FREDERICK ALLPRESS.

By the action of iodine monochloride or monobromide on triphenylbismuthine, iodobenzene and diphenylchlorobismuthine, BiPh<sub>2</sub>Cl, or diphenylbromobismuthine respectively are produced.

Diphenylchlorobismuthine (m. p. 184–185°) has also been prepared from triphenylbismuthine and bismuth chloride, and by boiling triphenylbismuthine dichloride with benzene.

By the action of iodine on triphenylbismuthine, iodobenzene, diphenyliodobismuthine, and a red compound containing more than 50 per cent of iodine are formed. The latter undergoes decomposition on extraction with hot benzene, yielding bismuth iodide.

With cyanogen iodide, triphenylbismuthine gives theoretical yields of iodobenzene and diphenylcyanobismuthine, BiPh<sub>2</sub>CN, which melts and decomposes at about 210°.

When tri- $\alpha$ -naphthylbismuthine reacts with iodine, a portion is converted into idonaphthalene and bismuth iodide, whilst some of the bismuthine is recovered unchanged.

With iodine monochloride or monobromide at least 75 per cent of the theoretical yield of idonaphthalene is obtained, and this is also formed by the action of iodine monochloride on diphenyl- $\alpha$ -naphthylbismuthine.

Iodine monochloride and diphenylbromobismuthine interact with the production of iodobenzene and phenylchlorobromobismuthine.

#### DISCUSSION.

In reply to Dr. Forster, Dr. CHALLENGER stated that the experimental difficulties connected with the manipulation of the trialkylbismuthines were considerable, and that in the presence of air these substances could not be prepared by the action of magnesium alkyl haloids on bismuth bromide, owing to oxidation. The same was true of the action of magnesium benzyl chloride and magnesium cyclohexyl bromide.

Attempts to prepare diphenylethylbismuthine by the action of magnesium ethyl bromide on diphenylbromobismuthine led to the formation of triethyl- and triphenylbismuthines.

290. "The Reduction of Cupric Salts by Sugars." By WILLIAM CRAMER.

The reduction of cupric salts by sugars in alkaline solution proceeds readily as far as metallic copper. The formation of cuprous oxide, which is usually regarded as the end-point of the reaction, is only an intermediate stage at which the reaction may be stopped by using an excess of the cupric salt.

291. "Some Properties of Solutions of the Boric Acids in Alcohol. A Modified Boiling-point Apparatus." By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

A form of boiling-point apparatus was described by which trustworthy and steady readings may be obtained. It is found that the addition of small quantities of ortho- and meta-boric acids and boron trioxide to ethyl alcohol causes a lowering of the boiling-point. The volatilities of solutions of these three substances in alcohol have been measured, and it is found that the effect on the boiling-point is least with the most volatile solute and *vice versa*.

292. "A New Method of Preparing Alkylated Sugars." By WALTER NORMAN HAWORTH.

The methods hitherto available for the alkylation of sugars and the simple carbohydrates generally have involved the application of alkyl iodides and dry silver oxide; which reagents were first employed for the etherification of sugars by Purdie and Irvine (*Trans.*, 1903, lxxxiii., 1021).

It has now been observed that practically all the methylated sugar derivatives obtained in the St. Andrew's laboratories during the past twelve years can be prepared conveniently and expeditiously by the agency, under carefully chosen conditions, of methyl sulphate and commercial sodium hydroxide. Other sugar derivatives, not previously described, have also been prepared by this method.

An important fact, which emerges as the result of this investigation, is, that methylation of the hydroxyl groups of a sugar-chain proceeds in definite stages, certain groups displaying a tendency to undergo etherification in preference to others. These partly methylated sugars are well characterised, homogeneous substances, which are formed as intermediate stages of the methylation process. The subjoined list of compounds, which were described, serves to illustrate this point:—

Heptamethyl sucrose .. .. .	b. p. 193°/0.18 mm.
Octamethyl sucrose .. .. .	b. p. 176°/0.05 mm.
Tetramethyl methylglucoside ..	b. p. 108°/0.1 mm.
Trimethyl methylglucoside ..	b. p. 124°/0.1 mm.
Tetramethyl glucose .. .. .	m. p. 84°.
Tetramethyl methylgalactoside..	b. p. 110°/0.15 mm.
Trimethyl methylgalactoside ..	b. p. 154°/18 mm.
Tetramethyl methylmannoside ..	b. p. 110°/0.33 mm.
Trimethyl methylmannoside ..	b. p. 155°/16 mm.
Dimethyl salicin .. .. .	m. p. 122°.
Monomethyltartaric acid .. ..	m. p. 174°.

and various methyl derivatives of mannitol and lactose.

These substances have been characterised by their various physical properties, and with this improved means of preparation they are now rendered easily

accessible for purposes of synthetic and other work which is in progress.

293. "The Rate of Saponification of Derivatives of Ethyl Benzoate." By HAMILTON MCCOMBE and HAROLD ARCHIBALD SCARBOROUGH.

The rate of saponification of derivatives of ethyl benzoate by potassium hydroxide in absolute ethyl alcohol has been studied at 30°. The influence of halogen substituents is to raise the velocity of saponification in comparison with the unsubstituted ester, whilst hydroxyl, amino- and methyl groups have a strong retarding effect. The values obtained for bromo-substituted esters are a mean between those for the corresponding chloro- and iodo-derivatives, even in the exceptional case of the para-substituted compounds, where the iodo-ester is saponified more rapidly than the chloro-compound.

The influence of water on the rate of saponification of ethyl benzoate was also studied, and it was found that on increasing the quantity of water, the value of  $k$  increased as follows:—

In absolute alcohol,  $k = 0.00543$ .  
In 73.4 per cent alcohol,  $k = 0.081$ .  
In 60.0 per cent alcohol,  $k = 0.148$ .

294. "Contribution to our Knowledge of Semicarbazones. Part IV. Action of Hydrogen Chloride." By FORSYTH JAMES WILSON, ISIDOR MORRIS HEILBRON, and MAGGIE MILLEN JEFFS SUTHERLAND.

The action of hydrogen chloride on varying types of semicarbazones and phenylsemicarbazones results in the formation of coloured or colourless salts containing 1, 1½, 2, or 2½ molecular proportions of hydrogen chloride, which show different degrees of stability. The monohydrochlorides are more stable than the dihydrochlorides, whilst those containing molecular proportions of hydrogen chloride intermediate between 1, 2, and 3 are extremely unstable and tend to lose hydrogen chloride, giving stable monohydrochlorides. For example,  $\alpha$ -piperonylidene-acetonesemicarbazone gives an unstable, vermilion salt containing 2½HCl, which rapidly loses hydrogen chloride until 1½ molecular proportions are lost, when a stable, orange salt is obtained. Acetonesemicarbazone gives a colourless salt containing 1½HCl, which is very unstable, tending to form a stable salt containing 1HCl. Salts were prepared from cinnamaldehydesemicarbazone, acetonesemicarbazone, acetophenonesemicarbazone, and benzaldehydesemicarbazone, and also from the corresponding phenylsemicarbazones.

295. "Attempts to Resolve Metallic Salts of Amino-acids and other Co-ordinated Compounds." (Preliminary Note). By THOMAS VIPOND BARKER.

Since the publication of a previous paper on co-ordination, isomerism, and valency (*Trans.*, 1912, ci., 2484), the author has been engaged in attempts to effect certain optical resolutions in the province of co-ordinated compounds. In view of the fact that the anticipated molecular configurations present some novel features of interest, which may have applications in other branches of chemistry, it is possible that a short notice may be of some value to other workers. Further, the fact that the attempted resolutions have so far been unsuccessful, makes it likely that two or three years may elapse before the author has had time to work through the whole of the material he has in view, which circumstance makes it desirable to issue a preliminary note.

One of the most remarkable successes that has attended the application of Werner's theory of subsidiary valency is the satisfactory theoretical interpretation it provides for the abnormal character of many complex salts. The violet-blue colour of the copper salts of glycine and of certain other amino-acids is accompanied by an abnormally low electrical conductivity in aqueous solutions; the latter anomaly is also characteristic of the corresponding salts of tervalent cobalt, and has led Ley to the conclusion that the nitrogen atom of the amino-group is com-

bined to the metal by virtue of a subsidiary valency, whereby a cyclic structure is produced. The graphic formula of copper glycine may therefore be represented

thus:  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{Cu} \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ , which it will be convenient to abbreviate to—

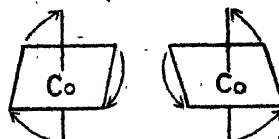


in which the arrow head denotes the nitrogen attachment.

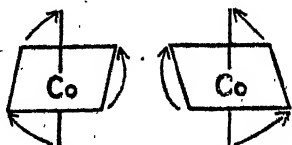
Now if the above formula is spacially contained in a single plane there is obviously no prospect of molecular enantiomorphism, but if, as seems likely, the four points of attachment are tetrahedrally arranged round the copper, the configuration is not identical with its mirror image. Any successful resolution, then, of copper glycine into optically active components would involve the definite proof that Ley's interpretation is correct, but it would also have the following additional and, in the author's opinion, more fundamental consequences: (1) Although everyone is forced to admit that Werner's resolutions prove the subsistence of enantiomorphous configurations, there appears to be some reluctance in accepting all the theoretical consequences, or, at any rate, those involved in Werner's interpretation. In so far as this reluctance is due to the fact that there is in every one of Werner's cases an unco-ordinated part, the chemical relation and spacial position of which, with regard to the nucleus, are quite vague, there could be no such scepticism in a case like copper glycine, since every part of the formula, except the nitrogen attachment, is precisely settled by the structure theory of organic chemistry, and molecular enantiomorphism would in itself demand this nitrogen attachment. (2) Although enantiomorphous, the molecule would contain no asymmetric atom, for the copper would possess a two-fold axis of symmetry; the whole molecule would really present an instance of Werner's so-called "molecular asymmetry I," which term is, however, obviously misleading since the molecule is symmetrical.

It need scarcely be emphasised that the same enantiomorphous features are theoretically realisable in the copper (nickel, palladium, platinum) salts of the homologues of glycine. Moreover, it is possible to foresee additional items of interest: with sarcosine,  $\text{CH}_3 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , the nitrogen would be united to four different groups, which, if tetrahedrally arranged, will confer on it asymmetry. Again, with  $\alpha$ -alanine there is a theoretical augmentation of the number of isomerides: if a  $d$ - and an  $l$ -molecule unite with the same copper, internal compensation will be prevented by the tetrahedral arrangement, and there may therefore be two pairs of enantiomorphous configurations, *Cu**dd*, *Cu**ll*, and *Cu**dl*, *Cu**ld*.

With regard to the salts of the tervalent metals, it may be mentioned that Ley actually obtained two "stereoisomerides," one of which he referred to a *cis-trans*-form of the octahedral structure. This supposition is somewhat unlikely and entirely unnecessary, for two stereoisomerides, each endowed with enantiomorphous possibilities, are realisable by the employment of *cis*-configurations, owing to the fact that the group  $\text{—NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{—}$ , unlike ethylenediamine,  $\text{—NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2\text{—}$ , is in itself unsymmetrical. Thus we may have—

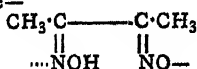


Enantiomorphous pair of symmetrical cobalt glycine.



Enantiomorphous pair of unsymmetrical cobalt glycine.

Very similar features of theoretical interest may again be expected in the class of the metallic dithiocarbamates about which there can scarcely linger any constitutional obscurities in view of the very convincing work of Delépine. These substances possess considerable crystallising powers, a fact which the author has been able to verify. Finally, there is the very important group of compounds, investigated by Tschugaeff, which may be represented by formulæ of the types  $\text{Pt}(\text{DH})_2$  and  $\text{Co}(\text{DH}_2)_3$ , in which DH signifies the following residue of diacetyldioxime—



Although many other cases could be cited, the above enumeration would appear to complete the list of substances which may be considered suitable, both by reason of their accessibility and crystallising power. The author would emphasise the fundamental feature common to all, namely, their neutral character, which has its origin in the perfect saturation of all the valencies, both principal and subsidiary, within the co-ordination sphere. Although obviously enhancing the theoretical value of any optical resolution, the neutral character of the substances in question introduces considerable difficulties in the technique, for the employment of an optically active base or acid is out of the question. There only remains the method of spontaneous crystallisation, or, in other words, the chance that the substances may resolve themselves. As already mentioned, no positive success can be recorded up to the present; certain of the substances, including the stereoisomeric cobalt glycines, have been definitely abandoned.

In conclusion, it may be pointed out that the above stereochemical considerations lead immediately to the theoretical possibility of a novel kind of molecular enantiomorphism amongst organic substances. Thus a

compound of the type  $\begin{array}{c} \text{CP}_2 \quad \quad \text{CO}_2 \\ | \quad \quad | \\ \text{C} \\ | \quad \quad | \\ \text{CO}_2 \quad \quad \text{CP}_2 \end{array}$  although possessing

a symmetrical configuration, is nevertheless enantiomorphous. If the chemist will accept the only precise meaning that can be given to the term "asymmetric atom," namely, an atom devoid of all symmetry, he will doubtless come to the conclusion that the above type of structure contains no asymmetric atom.

296. "Synthesis of Pinacones." (Part II.). By WILLIAM PARRY.

The action of sulphuric acid on some of the unsymmetrical pinacones described in Part I. (*Trans.*, 1911, xcix., 1169) has been studied.

(i) *δδ*-Dimethylhexan- $\gamma$ -one,  $\text{CMe}_2\text{Et}\cdot\text{COEt}$ , obtained when  $\beta$ -methyl- $\gamma$ -ethylpentane- $\beta\gamma$ -diol is heated with dilute sulphuric acid, is a colourless oil with an odour of peppermint, boiling at  $148\text{--}152^\circ/773$  mm. On oxidation with chromic acid mixture it yields (i.) carbon dioxide, (ii.) acetic acid, (iii.)  $\alpha\alpha$ -dimethylbutyric acid,  $\text{CMe}_2\text{Et}\cdot\text{CO}_2\text{H}$ , thus proving its constitution.

(2) *αα*-Dimethyloctan- $\delta$ -one,  $\text{CMe}_2\text{Pr}\cdot\text{COPr}$ , obtained by the action of cold concentrated sulphuric acid on  $\beta$ -methyl- $\gamma$ -propylhexane- $\beta\gamma$ -diol, is a colourless oil with a faint odour of peppermint, and boils at  $182\text{--}186^\circ/765$  mm. The semicarbazone forms white needles, melting at  $145^\circ$ .

The constitution of the pinacolin is proved by its oxidation to (i.) acetic and propionic acids by chromic acid

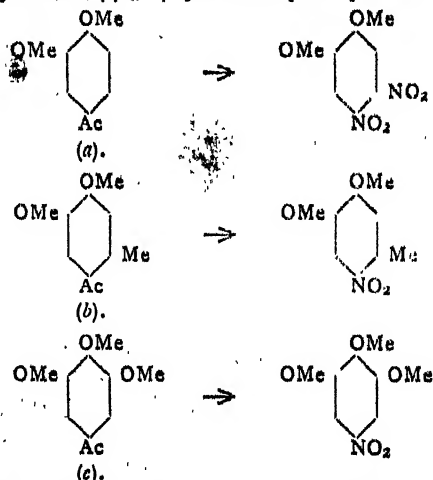
mixture, (ii.)  $\alpha\alpha$ -dimethylvaleric acid,  $\text{CMe}_2\text{Pr}\cdot\text{CO}_2\text{H}$ , by chromic acid in glacial acetic acid.

(3) The pinacone,  $\text{OH}\cdot\text{CMe}_2\cdot\text{C}(\text{C}_3\text{H}_7)_2\cdot\text{OH}$ , is obtained by the interaction of magnesium isoamyl bromide and ethyl  $\alpha$ -hydroxyisobutyrate; it forms white, waxy needles, melting at  $34\text{--}35^\circ$ . By cold concentrated sulphuric acid it is converted into *ββ*-(4-tetramethyldecan-1-one,  $\text{C}_5\text{H}_{11}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{C}_5\text{H}_{11}$ , a yellow oil, boiling at  $132\text{--}134^\circ/25$  mm., which does not form a semicarbazone. The constitution of this pinacolin is proved by its oxidation to (i.) isovaleric acid, by chromic acid mixture; (ii.)  $\alpha\alpha\delta$ -trimethylhexoic acid,  $\text{C}_5\text{H}_{11}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , by chromic acid in glacial acetic acid.

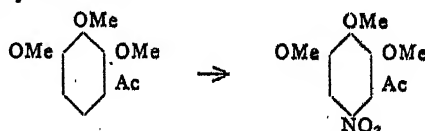
(4)  $\gamma\gamma$ -Diphenylbutan- $\beta$ -one,  $\text{CMePh}_2\cdot\text{COMe}$ , is obtained as a yellow oil, b. p.  $180^\circ/18$  mm., when  $\alpha$ -diphenyl- $\beta$ -methylpropane- $\alpha\beta$ -diol is heated with dilute sulphuric acid. It solidifies when seeded with a crystal of the acetophenonepinacolin described by Thoenner and Zincke (*Ber.*, 1878, xi., 1989), and then melts at  $41^\circ$ , thus proving the identity of the two pinacolins. Further confirmation of this identity is afforded by the oxidation of the yellow oil to  $\alpha\alpha$ -diphenylpropionic acid,  $\text{CMePh}_2\cdot\text{CO}_2\text{H}$ , by chromic acid mixture.

297. "Substitution in Aromatic Hydroxy-compounds. Part II. Acetyl-nitro-substitution." By VICTOR JOHN HARDING.

An account was given of the action of nitric acid on various methoxyacetophenones. In those cases where the acetyl group occupies a position which, in the parent phenol ether, is active to nitric acid, it is found that the acetyl group is displaced by the nitro-group. This is termed acetyl-nitro-substitution. The following acetophenones are found to undergo this substitution: (a) 3:4-dimethoxyacetophenone, (b) 4:5-dimethoxy-*o*-tolyl methyl ketone, (c) 3:4:5-trimethoxyacetophenone:



Where the acetyl group occupies a position which, in the parent phenol ether, is inactive to nitric acid, it is found that a nitroketone is produced. Thus 2:3:4-trimethoxyacetophenone on nitration gives 6-nitro-2:3:4-trimethoxyacetophenone, and not 4-nitropyrogallol trimethyl ether:



## MEETINGS FOR THE WEEK.

WEDNESDAY, 13th.—Royal Society of Arts, 5. (Juvenile Lecture) "How to Sing a Song," by H. Plunkett Greene

# THE CHEMICAL NEWS.

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## TARIFFS, FREE TRADE, AND INDUSTRY.\*

By J. TAYLOR PEDDIE, F.S.S.

THE problems of Tariffs and Free Trade have always afforded keen subjects for debate in and outside Parliament and amongst individuals. But the one outstanding feature in all the debates and discussions that have taken place is the extraordinary explanations that have been given by the average politicians in favour of their theories. We are reminded of the truism we have read somewhere, that "explanations do not survive; it is the things which are explained."

In discussing such highly technical subjects one would have imagined that the solutions, if such were required, would have been left to the technologist. If we desire to be cured of any physical weakness we go to our family physician; if we require information upon any subject relating to chemistry we go to the chemist; if we require advice on banking we go to the banker; and in engineering we go to the engineer. But on the subject of tariffs or free trade we go to the politician, and believe he possesses the last word in political economy, or, as it is now termed, National Economics. The specialist is not considered or consulted in this sphere of activity.

We are not now offering criticism against the views of either Free Traders or Tariff Reformers, but merely endeavouring to demonstrate that the regulation of the working conditions in which industry operates should be left to the technologist. The standardisation of these working conditions are much too complex for the ordinary layman to solve or appreciate. It is difficult to understand why such important business questions as these have been left in the cockpit of party politics so long; perhaps it is due to our admittedly weak educational system, but whatever the cause it must be removed. It is quite clear that no definite line can be drawn across the centre of these problems; viewed from the standpoint of business they are indivisible questions, and any difficulty that may arise thereunder should be considered purely on its merit, upon the employment it will give to labour, and upon the reflex action it may have on the other industries.

We are not inclined to wholly agree with the view of J. B. Say, that the history of political economy is of little value, being for the most part a record of absurd and justly exploded opinions. History has a good deal to teach us as to the manner by which we have arrived at our present position. If any fault is to be found on the historical side, it may be found in the fact that the study of the science of political economy has not reverted to the technologist sooner. Our general knowledge of economics has for the most part come to us from authors who have been largely engaged in the development of political constitutions, and which, incidentally, has led to a study of the conditions that were requisite to improve the lot of the individuals in the State. But we have to be thankful to the political economists for such knowledge as we possess, even although many of their theories have been exploded.

The world's industry has grown up under the guidance of the political economists of the kind described; but with the advance of science and education conditions have necessarily changed. The leading industrialists of to-day, owing to the advance of science and education, now hold superior positions, and are consequently in a position to state precisely what working conditions are essential to procure the maximum production of wealth from industry.

Such criticisms as we have to offer, of course, refer only to the working conditions surrounding our own industries, and not to those surrounding German industry, in which latter country theoretical views have long since been discarded for the technical and practical.

The Germans have been quietly aggressive in this sphere of activity for some considerable time, but they are not to be blamed for that; rather are they to be commended. Had German Industrialists not allowed German Military Society to remain supreme, they would undoubtedly as a nation have gained supremacy in production; but, tied to the Military school, and obsessed with the idea that such attachment would seal the fate of Great Britain and France, and ultimately lead to considerable expansions of their businesses, have lost them their opportunity, and they richly deserve their fate. German Industrialists ought to have realised that the supremacy of Militarism leads to a low estimate of industry, and those engaged directly or indirectly in it. Not only that, but industry is made to slave for militarism when the latter is supreme; it can be seen, therefore, that such a condition of affairs is a relic of ancient and mediæval history, and certainly not suitable for this age of enlightenment; but it would not be possible under the Democratic and Monarchical style of government, such as we have in Great Britain. It is only possible under Absolute Monarchism.

In Sir William Ramsay's short thesis on "German Methods in Commerce," issued by the Institute of Industry and Commerce, he states that "the German military organisation had its counterpart in their commercial organisation; that there exists an Imperial Council, whose proceedings are kept quiet, but which takes into consideration all obtainable statistics, and, as far as possible, legislates, or endeavours to legislate, on the basis of these statistics. Where fiscal duties are found to be required, such a Council puts them on; where there is an advantage in taking them off, they are removed. Where cheap transit is possible they give it, for the railways are the property of the State." Sir William Ramsay further adds:—"Is it to be expected that any country can fight such a combination as that without adopting, at all events, something of their methods, or without studying their methods, and without combining together, if not to imitate them, at least to thwart them?"

This knowledge has been known in a limited circle in Britain for some years past, but the voices that issued the warnings were crying in the wilderness of apathy. The average Britisher exhibits a horribly apathetic attitude towards conditions which exist outside of his own business, and it is to be hoped that the Great War will now open up his mind to the fact that national organisation in industry is as essential as the national organisation we now have in our military and naval forces. The formula of organisation within organisation must be studied, and the working conditions which are necessary to make it a success.

A proper study of the science of production, distribution, and management, however, cannot be effected without considering the relations of Free Trade and Tariffs thereto; they form part of the whole question. But certain essentials require to be defined in order to clear the ground and open up the field to impartial consideration, and in doing this we fulfil the purpose of this article.

At Free Trade and Tariff Reform meetings politicians are often asked the question, "What is raw material?" To very many the question is a thorny one, and the explanations often given have seldom been convincing. We trust politicians will take no offence at these remarks; they are put forward as evidence only against the continuance of the present system. The proper interpretation of "What is raw material?" is as follows:—Raw material is the agent of production—i.e., substance or matter in its lowest form of utility, such as iron ore, cow hides, raw cotton, coal, corn, wheat, barley, tea, coffee-beans, cocoa-beans, oil, &c., &c., and the moment either of these sub-

\* Read at the Institute of Industry and Commerce.

stances is subjected to a development process, which implies the inclusion of labour, it ceases to be raw material and becomes material. The intermediate stages have always been overlooked, and the distinction must be carefully noted. Examples are given as follows:—Iron ore is a raw material, the pig iron produced therefrom is material; the steel produced from the pig-iron is still material, or may be termed advanced material; the machine produced from the steel is not looked upon as material, but as an article of utility. In other words, the more labour that is employed in the converting processes the more do you get away from the raw material stage. To bring it nearer home we will take the case of cow hides; these are raw material, but the moment they are converted into leather they become material, and the moment leather is converted into boots, what do you call them? Not raw material, material, or advanced material, but boots—articles of utility, made to satiate the wants of man.

To make the point a little more clear, the following quotation from the book written by Prof. Charles Lee Raper may be helpful, namely:—"The vast quantities of raw material which are supplied by the agriculturist and miner must be transformed into higher form utilities before they can be of the greatest service and pleasure to man. The consumer does not eat wheat in its raw or elementary form. It must be transformed by the miller into flour, and the flour must be converted into bread. Raw cotton fibre cannot satiate man's want for clothing. It must be carded, spun, and woven; it must be made into some form of cloth before man wears it upon his body. From the cotton fields it must go to the gin, where the fibre is straightened; from the carding-room it must go to the spinning machine, where this straightened fibre is stretched and twisted into thread or yarn; from the spinning machine it must go to the loom, where it is woven into cloth; from the weaving-room it must go to the bleaching and dyeing rooms, where it receives the desired colours. In all these stages is the manufacturer; in all of these stages is the man who, by means of all of the agents of production, transforms, time and again, the elementary forms of cotton until they become the thousands of varieties of the higher forms of cotton fabric. This life-history of the cotton fabric is substantially the life-history of every other kind of finished goods. As we have already said, production is a process of creating forms of things, not material things themselves. The agriculturist and miner produce forms of utilities, or wealth, which we call elementary. The manufacturer changes these elementary forms into higher forms; he creates the higher form utilities."

The importance of this great question to labour and capital, therefore, will, we hope, not be overlooked, for they are the forces directly concerned. The interests of both in questions relating to production, and especially in the acquisition of raw material, are identical. Any question which may prejudicially affect one interest must affect the other interest. So we come to see how essential it is that all the forces employed in industry should be co-operative, and also that the formula of organisation within organisation on national lines is as beneficial to the one as it is to the other.

Another important question asked by Tariff Reformers and Free Traders is the following: "Is the burden of a tariff entirely borne by the consumer, or is it entirely borne by the manufacturer responsible for the shipment of the goods?" It may seem paradoxical, but the reply to this question follows the reply given to "What is raw material?" One is a corollary of the other, and the answer may be given as follows, namely:—If a tax is imposed on what is herein defined as raw material the consumer pays the tax. But a tax imposed on material or other articles of utility is paid by the shipper in the country of origin. The reason why this is so is that labour cannot compete with nature in the production of minerals or food products, but labour can compete with labour in the de-

velopment of raw material into higher-form utilities. Therefore, it must not be assumed that in the purchase of material or other articles of utility the consumer, by being limited to a given source for the satisfaction of his requirements, must pay more in consequence. To more clearly define the point; it may be stated that a machine tool can be purchased as cheaply in America, notwithstanding the high American duty, as it can be in England, and in some cases cheaper. If a British machine-tool manufacturer desires to compete in America he must pay the cost of the American duty; the cost of production in America is about equal to that prevailing in England—hence the reason; and it is attributable to the fact that labour competes with labour. The Ford motor car is manufactured and sold more cheaply in America, with a substantial margin of profit, than any car of a similar kind can be manufactured and sold in England—for the same reason.

American manufacturers of articles of utility do not hope to increase the price of their production by the amount of the tariff or any portion thereof, and the same argument applies to other manufacturers in other countries; but it can be assumed that in the purchase of tea the consumer must pay any import tax that is imposed, for the reason, as already stated, that labour cannot compete with nature in Ceylon and other Eastern countries in the production of tea; supply is limited to a season's crop.

It is the duty of the State, therefore, to ensure that no monopoly is created in the supply of any given kind of raw material, and to ensure that no tariff duty is imposed on the importation of it; but this statement, as already indicated, does not apply to material, advanced material, or other articles of utility in cases where it may be considered necessary. The latter proposition is safeguarded by the first.

There are certain wealthy corporations which exist for the purpose of creating monopolies in what is herein termed as raw material; but these should be broken up by the State, for they are a menace to cheap production. The community at large pay them huge profits to which they are not entitled. On the other hand, large corporations which exist for the purpose of developing material, advanced material, or other articles of utility should be left alone, for it is impossible for them to create monopoly prices and unreasonable profits, for the reason that labour competes with labour. Whatever profits may be earned by the latter group may be considered as being the reward of enterprise. If profits are continuously large competition will set in, and profits will become reduced in proportion to the extent of the competition.

It will now, we hope, be seen that the questions we are now discussing properly belong to and form part of "First Principles of Production," and we trust that the consideration now given to them may be instrumental in relegating their future development to the technologists. As we have already stated, viewed from the standpoint of industry the problems of Free Trade and Tariffs are indivisible questions, and the problem as to whether one side or the other is of the most benefit to industry should not be left to the ordinary layman to decide, but to the leaders of industry in consultation with the Government.

Cultivation of Medicinal Plants for the Drug Market.—The attention of all who are interested in this subject may be called to an article thereon by Dr. W. W. Stockberger, the physiologist in charge of Drug-plant and Poisonous-plant Investigations, Bureau of Plant Industry of the United States Department of Agriculture, which is published in the *American Journal of Pharmacy* for November, 1914. Although the author does not enter into great detail he corrects some popular errors concerning the scope and function of such gardens, and makes some suggestions which may extend their usefulness.



ON SALTS COLOURED BY CATHODE RAYS.\*

By Prof. E. GOLDSTEIN.

PERHAPS a part of the phenomena which I am about to discuss is already familiar to you all. I shall not bring forward many hypotheses. So you will, perhaps, ask why I should speak at all. And, in fact, apart from reference to certain facts not published hitherto, my intention is mainly to invite the interest of men younger and abler than myself in a class of phenomena which seem to constitute a new condition of matter, but on which very few have yet worked.

If cathode rays fall on certain salts—for example, common salt, or chloride of potassium, or potassium bromide—vivid colours are produced immediately on these salts (E. Goldstein, *Wiedem. Ann.*, liv. 371; lx., 491; *Phys. Zeitschr.*, iii., 149; *Sitzungsber. Ber. Akad. d. Wiss.*, 1901, 222). Thus common salt becomes yellow-brown (like amber), potassium chloride turns into a beautiful violet, potassium bromide becomes a deep blue colour quite like copper sulphate. Here you see a specimen of common salt transformed in this way on the surface of the single crystals into a yellow-brown substance. I show also sodium fluoride, which takes a fine rosy colour.

The colours so acquired in a very small fraction of a second may be preserved for a long time, even for many years, if the coloured substances are kept in the dark and at low temperatures; but in the daylight, and also under heat, the colours will gradually disappear until the original white condition is reached again.

The colours of different salts are sensitive to heating in a very different degree. I could show you the yellow sodium chloride, prepared some months ago in Europe, but I cannot show you here the violet KCl and the blue KBr, because these colours, even in the dark, do not stand the heat of the equator. The same salt, if dissolved, may keep very different colours; according to the medium in which it has been dissolved, even when the pure medium itself cannot be coloured at all by cathode rays. I am speaking of *solid solutions*, produced by fusing a small quantity—for instance, of common salt, or of certain other alkali salts—together with a great mass of a salt which remains itself colourless in the cathode rays, as, for example, the pure potassium sulphate. Lithium chloride acquires a bright yellow colour in the cathode rays, but if dissolved in potassium sulphate a lilac hue is produced, as you may see in this specimen. Likewise the pure carbonate of potassium acquires a reddish tint, but after dissolving it in the potassium sulphate it becomes a vivid green in the cathode rays, as you see here.

Very small admixtures are sufficient to produce intense colours. So 1/25,000 of carbonate will produce the green colour in the potassium sulphate; even 1/100,000 gives a marked colour, and an amount of certain admixtures, which I estimated as 1/1,000,000 only, may produce a slight but quite perceptible coloration in some salts. So if you work with potassium sulphate which you obtain from chemical factories guaranteed as chemically pure you may observe a set of different colours in these preparations under the cathode rays, by which you will detect the nature of the different small admixtures which adhere to the pretended pure preparations of the different factories. In this way a new analytical proof, much more sensitive than the ordinary chemical methods, is obtained, and impurities may be detected even when a certain specimen of salt contains more than a single impurity, because the colours produced by different admixtures generally disappear with different speed in the daylight or under rise of temperature. For instance, the ordinary potassium sulphate turns to a dark grey with a slight greenish tint at first. After a short while the very sensitive grey will disappear, simply under the ordinary temperature of the laboratory

room, and a vivid green comes out. The grey hue indicates a very small amount of sodium chloride, 1/100,000 or so, and the remaining green indicates the admixture of a carbonate. Here are some preparations of potassium sulphate, each containing a single small admixture ( $K_2CO_3$ ,  $Li_2CO_3$ , LiCl, KCl, KBr). You will notice how different are the colours of the originally white substance, varying from green to bluish-grey, ash-grey, greyish-blue, and violet.

By fractional crystallisation one may finally get a really pure preparation of potassium sulphate, which is no longer coloured by cathode rays (or only in a very slight degree, indicating minimal traces of sodium chloride). But there are other preparations which, so far as I know, cannot be acquired in pure condition by any means, not even by fractional crystallisation. I never came across a pure sodium sulphate—the purity exists only on the manufacturers' labels. Even the best preparations of this salt contain an amount of sodium carbonate which up to the present cannot be separated from it, not even by frequent fractional crystallisation. The colour produced by the small admixture, which always remains, is a very marked ash-grey. By an intentional further addition of sodium carbonate the colour becomes nearly black.

The question arises: What may be the cause of these colourations in pure salts and also in solid solutions of them? Shortly after the colours of the alkali salts had been discovered an explanation was given (E. Weidemann and G. C. Schmidt, *Wied. Ann.*, liv., 618), according to which the phenomenon mainly consists in a chemical reduction. For instance, in the case of potassium chloride the chlorine would be set free, while the remaining potassium is dissolved in the unaltered main quantity of the salt, colouring it at the same time. And it seemed a convincing proof for this theory when Giesel (*Ber. D. Chem. Ges.*, xxx., 156), and also Kreutz, simply by heating rock salt in the vapours of sodium or of potassium, produced colours in this rock salt quite similar to those produced by cathode rays. It seemed that the problem was settled finally. However, it was soon discovered that the coloured Giesel salts, although they look to the eye quite like the cathode-ray salts, in all other respects behave quite differently. For instance:—

(1) The cathode-ray salts, as I mentioned before, are very sensitive to daylight; after an exposure to diffuse daylight of a few minutes—or in some salts even of several seconds only—the coloration diminishes, whilst the Giesel salts remain unaltered even when they are kept in full sunshine for days, or even weeks.

(2) The cathode-ray salts, if dissolved in distilled water, show absolute neutral reaction; the Giesel salts are strongly alkaline.

(3) The cathode-ray salts give very marked photo-electric effects, as Elster and Geitel (*Wied. Ann.*, lix., 487) observed; the Giesel salts are quite ineffective.

(4) In certain circumstances, which will be mentioned further on, the cathode-ray salts may emit a phosphorescent light, the Giesel salts none at all; therefore the question arose again, whether there is not a marked internal difference between the cathode-ray salts and the Giesel salts, and what is the nature of the latter?

I have succeeded in settling this question, having produced salts by cathode rays, the behaviour of which is in every respect absolutely identical with that of the Giesel salts. You may produce such substances if you allow the cathode rays to fall on the original salts, not for a short moment only, but for a somewhat prolonged time, *until the salts are strongly heated*. Produced in this way the salts will keep colours, but the substances coloured in this way are not sensitive to light; they show no photo-electric effect; they give strong alkaline reaction, and they are not suited for phosphorescence—all like the Giesel salts. It is quite sure, and you may test it also directly by spectroscopic proof, that in this case, if, for instance, you have worked on sodium chloride, the chlorine is set free. Then, of course, an amount of free sodium is left, which dis-

\* A Paper read before Section A. of the British Association at the Australian meeting, and ordered by the General Committee of the Association to be printed in *extenso*. From *Nature*, xciv., No. 2337.

solves itself in a deeper layer of unaltered sodium chloride, to which the cathode rays could not penetrate. I call these non-sensitive colours the *after-colours of the second class*, while the ordinary sensitive after-colours, produced in a short time on cool salts, are called after-colours of the first class.

Now, if the after-colours of the second class are identical with those of the Giesel salts, then, of course, the very different substances of the first class cannot be also identical with the Giesel salts. Therefore the question arises anew, what is the nature of the first-class after-colours?

One observes with regard to solid solutions that the first-class colours depend not only upon the metal contained in the small admixture, but they vary greatly, for instance, in the case of the admixture consisting of potassium chloride or bromide or iodide. This indicates that the metals alone do not cause the after-colours. It becomes much more clear when we expose some ammonium salts to the cathode rays. (The ammonium salts are cooled by liquid air in the discharge-tube to prevent their evaporation). Then you get strongly-marked after-colours likewise; for instance, ammonium chloride becomes yellow-greenish, the bromide becomes yellow-brown, the iodide becomes brown, and the fluoride a deep blue. In the daylight these colours are gradually destroyed, quite like other after-colours of the first class. The colours themselves—yellow-greenish for the chloride, yellow-brown for the bromide, and so on—induce us to presume that the after-colours in this case are produced by the haloids and not by the hypothetical ammonium radicle. This presumption becomes a strong conviction when we observe that also a great number of organic preparations which contain no metal at all (and not any metal-like radicle) acquire marked after-colours of the first class in the cathode rays also. (The part of the discharge-tube which contains the organic substances is cooled by liquid air).

Then you may observe that solid acetic acid ( $C_2H_4O_2$ ) remains quite colourless in the cathode rays; but if you substitute a hydrogen atom by chlorine, the substance thus produced (the monochloro-acetic acid) acquires a marked yellow-green after-colour. If you introduce an atom of bromine instead of chlorine you get  $C_2H_3BrO_2$ , and the after-colour is of a marked yellow. Bromoform ( $CHBr_3$ ) turns into the colour of loam, and chloral ( $C_2HCl_3O$ ) becomes a deep yellow. In this way we see that not only salts, but likewise substituted acids, substituted hydrocarbons, and substituted aldehydes acquire after-colours if they contain any haloid.

Now, it seems highly improbable that in the case of alkali salts the electro-positive component is absorbed only (producing the after-colour), and that, on the other hand, in the ammonium salts and in the organic substances the electro-negative component is efficient only. The most probable inference is that in each case *both* components remain and that both are efficient, but that under the same conditions the haloids produce a slighter colour than the metals, so that in the case of the salts the haloid colour is overwhelmed by the metal colour.

Therefore we are compelled to suppose that we have not to deal with a decomposition in the ordinary form, by which the different components are finally separated from each other, and at least one of them is set entirely free, but that the components detained by absorption remain at a quite short distance from each other, so that they may easily meet again. I realise that—for instance, in the case of sodium chloride—at every point of the coloured layer there is an atom (or perhaps a molecule) of chlorine and an atom (or a molecule) of sodium; but they cannot combine, because they are fixed by absorption and distended from each other by the absorptive power, which in this case surpasses the chemical affinity. But the absorptive power may be weakened by heating and the chemical affinity or the amplitude of the molecular vibrations may be strengthened by the energy of daylight.

If we grant these assumptions it is immediately evident why the reaction of all dissolved colour substances of the first class is a neutral one, for the two components may combine again and re-establish the original substance. The other special qualities of the first-class colours, and especially their differences from the Giesel salts, which contain the electro-positive component only, may be deduced likewise from this retention of both components and their opportunity of meeting each other again when the absorptive power is weakened or the chemical affinity is strengthened. Now, the two components in the coloured substances being distended in some degree, I propose for this special condition of matter the name of *distention*. If we accept this, have we created a new name only, or does matter in this condition really show new qualities? It seems to me that we have to deal with a peculiar condition of matter, which deserves a more elaborate study than it has met until now. I will not enter again into some special qualities, which have already been mentioned—the photo-electric effect and so on—but I should like to point out that matter in the distention state shows a strongly strengthened absorption of light.

We noticed with regard to ammonium chloride the yellow-greenish after-colour of the chloride. Now, cathode rays, as used in these experiments, will not penetrate any deeper than one-hundredth of a millimetre into the salt. In such a thin layer even pure liquefied chlorine would not show any perceptible colour. But, besides this, it must be noticed that we observe this after-colour at the temperature of liquid air, and that chlorine at this temperature, as Dewar and Moissan observed, is snow-white, even in thick layers. In a similar degree the brown colour of bromine is weakened at low temperatures. Now if, nevertheless, we observe at this very low temperature the marked characteristic colours of chlorine and bromine, we must conclude that the absorptive power of these substances has become a multiple of its ordinary value. One may observe this strengthening of the absorptive power directly in the pure sulphur. Sulphur likewise turns into a snow-white substance if cooled by liquid air; but when the cathode rays fall on the white sulphur it takes immediately a yellow-reddish colour. It is a real after-colour, because at constant low temperature the colour is destroyed by daylight.

Now, since the strengthening of light absorption occurs in this elementary substance, it becomes evident that the cause cannot be any chemical process but only a physical allotropy. The special character of this allotropy (which may be connected with an absorption of electrons) will not be entered on in a discussion here. Probably we have to deal with a polymerisation, so that, for instance, the yellow-reddish sulphur would be analogous to polymerised oxygen—to ozone.

I have mentioned already that the first-class after-colours are gradually destroyed by incident daylight. A peculiar phenomenon is connected with this destruction of colour. I found that after the daylight had fallen on the coloured substances, even for the shortest time, most of them showed a marked phosphorescence of long duration. I have observed this phosphorescence even in substances which had been coloured twelve years ago and had been kept in the dark since that time. The diffused dim light of a gloomy November day, when falling through a window on the coloured substance for one or two seconds only, is sufficient for the production of this phosphorescence in a marked degree. If you allow the daylight to fall several times on the same spot, then the colour is weakened at this spot, and we come to the presumption that the loss of colouration is generally attended by the emission of phosphorescent light. This is in accordance with the experience of Wiedemann and Schmidt, that if the destruction of the colour is produced by heating, likewise a phosphorescent light is produced, which in this case is strong but of a short duration, corresponding to the quick destruction of the after-colours by strong heating.

If the salts, after having been coloured in the condition

of a fine powder, and then having been put between two glass plates (in order to obtain a plane surface), are placed in a photographic camera instead of the photographic plate, you may get a fine phosphorescent picture of a landscape or of architecture after a very short exposure.

Time does not allow me to mention in detail several other peculiarities which are shown by matter in the distention state. In one direction only I may be allowed to make some remarks.

The first-class after-colours may be produced not only by cathode rays but also by the  $\beta$  rays of radio-active substances, as you probably know. But they may also be produced by ultra-violet light—for instance, by ultra-violet spark light—even when a quartz plate is interposed between the spark and the salt. More than thirty years ago I brought forward a hypothesis, according to which in every point where cathode rays strike a solid body a thin layer of ultra-violet light-radiating molecules is produced in the gas, to which ultra-violet light of very short wave-lengths—for instance, the phosphorescence of the glass walls in the cathode rays, is due. But I came, further, to the assumption that nearly all effects which are commonly ascribed to special qualities of the cathode rays, and likewise of  $\beta$  rays and X-rays, are mere effects of the ultra-violet light which is produced by the stopping of these rays. I have been guided by this assumption during many years, and have very often been aided by it in foreseeing new phenomena. For instance, in this way I was induced to expect that the after-colours would be produced not only by cathode rays but also by the ordinary ultra-violet light; further, I could guess that also the X-rays would produce after-colours (which in this case have been observed by Holzknacht), and in recent times I could foresee that solid aromatic substances (the benzene derivatives) in the ultra-violet light must change their spectra of ordinary phosphorescence, composed of broad bands, and turn to peculiar spectra composed of narrow stripes, the wave-lengths of which are characteristic of the single aromatic substances (E. Goldstein, *Verhandl. d. D. Physik. Ges.*, xii.). So I believe, also, that the after colours are produced not directly by the cathode rays or by  $\beta$  rays, but by the aforesaid ultra-violet light which is connected with the stopping of the other rays.

In this way the after-colours enter at once into a great class of phenomena known as *reversible effects of light*. You know that certain effects of the visible spectral rays are destroyed by rays of longer wave-lengths, by the infra-red rays. And the analogy to this phenomenon is, in my opinion, the destruction of the after-colours; they are produced by the ultra-violet light of the stopped cathode rays, and are annihilated by the longer visible wave-lengths of daylight. In this way you may likewise understand, for instance, that the coloured spots, produced by X-rays on the luminescent screens after long exposure, may be destroyed again by exposure of the screens to daylight. You may also explain the peculiar medical observation that therapeutic radium effects in parts of the human body not covered, specially in the face, are often not of long duration, for the face is exposed to the counteracting visible rays of daylight.

We notice here a connection of our subject with a department of great practical importance. For all therapeutic effects of X-rays, radium rays, and mesothorium rays would, according to this view, be effects only of ultra-violet light produced by the stopping of these rays in the human body, and the special character of the radium and mesothorium and X-ray treatment would consist mainly in the carriage into the interior of the body by the rays of the ultra-violet light, which is not confined to the surface of the body, but is produced at every place where any of the entering rays are stopped. You may notice, further, that this view of the medical ray-effects presents a heuristic method for the treatment itself, which up to the present followed quite fortuitous and merely empirical paths; for it may be hoped that treatment by radio-active substances will be useful in every disease in which ultra-violet light

has been proved to be efficient in some degree. You will avoid such treatment in the well-known cases in which light of short wave-lengths is noxious, and you may be justified in substituting an ultra-violet light treatment where radium or mesothorium is not obtainable. At the same time it becomes evident why the treatment of certain diseases by the  $\beta$  rays has effects very similar to those produced by *fulguration*—that is, by the light of very strong sparks; the efficient agent is in both cases the ultra-violet light.

But it cannot be a physicist's task to enter too far in medical questions; it was only my intention to show how interesting are some of the problems which are connected with the salts coloured by cathode rays.

## THE WALDEN INVERSION.

By CECIL L. HORTON, B.Sc.

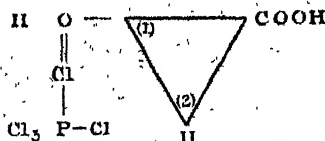
THE directive action of the carboxyl groups in this inversion was pointed out by the writer in the issue of the CHEMICAL NEWS dated July 25, 1913. Up to the present no theory has been put forward embodying this principle, and all the theories published have one weak point, namely, the fact that complete racemisation should take place.

In developing any theory three things must be carefully considered—

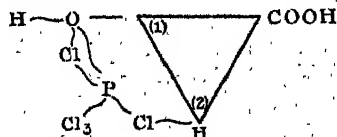
- i. The effect of the carboxyl groups, both when free and when in combination with the alcohol radicle.
- ii. The fact that all the substituents are unsaturated.
- iii. That all the reagents are unsaturated.  $\text{PCl}_5$ , which alone gives a constant reaction, is the least unsaturated member of the group, probably the saturation is almost complete.

A consideration of ii. and iii. points to the probability of the formation of an intermediate compound in the first case, the final position of the addendum depending upon the attractive or repulsive action of the carboxyl or ester.

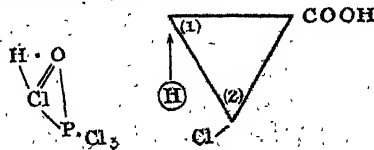
In the case of the action of phosphorus pentachloride on lactic acid, we have the formation of the intermediate compound—



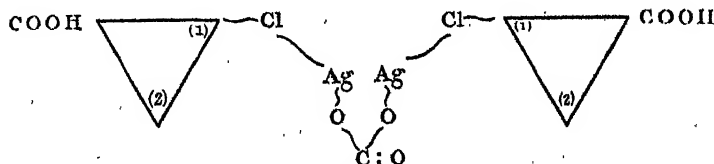
By reason of the length of the addendum chain, a chlorine atom comes very near to position (2). As the hydrogen and chlorine come together the following distribution takes place:—



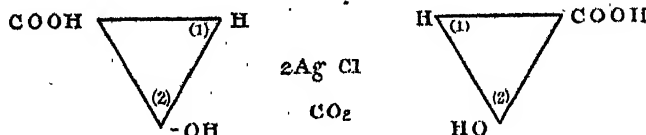
The momentary change in the valency bond (1) causes a temporary increase in (2), and hence the breaking of the bond between the carbon and the oxygen at (1) occurs at the same time as a linkage of the chlorine and carbon at (2). The position then becomes—







FORMULA A.

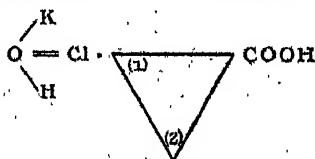


FORMULA B.

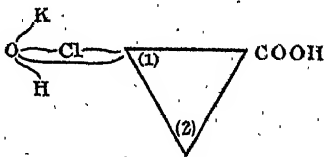
and the hydrogen migrates to (1). HCl splits off from the compound thus thrown off, leaving  $\text{POCl}_3$ .

Since the position taken up by the pentachloride is independent of any attraction or otherwise by the carboxyl group, it follows that the changing of the sign must be a constant result. The suggestion that the carboxyl has little effect on the position of the addendum is based on the chemical character of the pentachloride (and also on its saturated nature, in that the binding forces in the intermediate compound are weak).

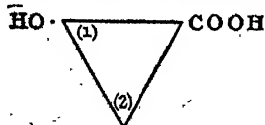
In the case of potassium hydroxide on  $\alpha$ -chloropropionic acid, the intermediate compound formed is—



As the potassium hydroxide comes into the sphere of influence of the chlorine atom, the chlorine and the oxygen tend to become connected. As the potassium comes nearer to the chlorine, more and more of the valency concentrates itself between the potassium and chlorine, and hence the combination between oxygen and potassium, oxygen and chlorine, and carbon and chlorine is weakened:—

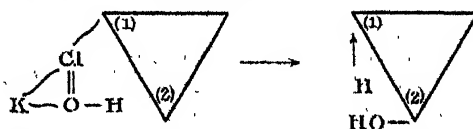


Since, however, the effect of the carboxyl radicle is to attract the addendum, and that of the methyl group to repel it more strongly, the tendency will be for that group to move away from position (2). The connection between the oxygen and carbon will take place at (1) in preference to (2), and therefore there will be no change in sign.



In the case of a *di*-acid, such as *d*-chlorosuccinic acid, the first stage will be as before. Now both the carboxyl groups will tend to attract this intermediate group; it will be constrained to move in such a way as to bring it nearer to (2). In this case the weakening of the bond (1) and

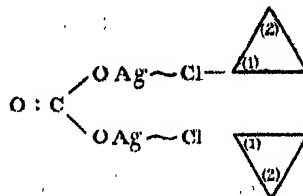
temporary redistribution caused in the valency of this carbon will cause position (2) to receive a portion of this momentary excess, and this excess of valency in the position (2) permits of a combination—



and hence there will be a change in the configuration.

The contradictory results obtained by the use of moist silver oxide can be accounted for in this manner. The silver oxide does not act in the same form as the alkali, in that in the experiment under consideration, the solution contained  $\text{CO}_2$ . The addendum will therefore take the

form  $\text{Ag}^+\text{O}^-$   $\text{C}=\text{O}$  and with  $\alpha$ -chloropropionic acid the intermediate compound will be—

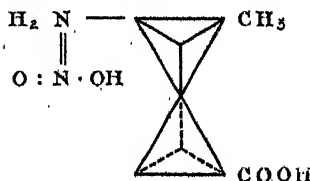


In this case the acid  $\text{O}=\text{C}-\text{O}^-$  is repulsed equally by

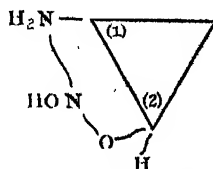
the carboxyl group in each of the original molecules, and hence the position (2) becomes the favoured one (see Formula A).

The compound so formed, under the hydrolysing action of water, becomes that shown by Formula B. The product thus obtained having an opposite configuration to that of the parent.

With regard to the action of nitrous acid on the amino acids, the probable course is as follows:—Taking as the first example the monobasic acid *d*- $\beta$ -aminobutyric acid, which, under the influence of nitrous acid, passes into the *l*- $\beta$ -hydroxy acid, the intermediate compound formed is—



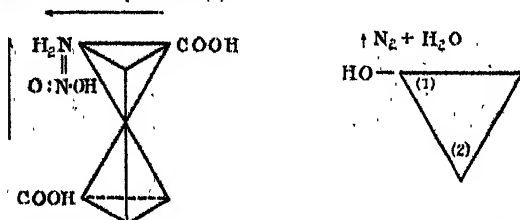
Now, it is highly probable that the negative radicle  $\text{COOH}$  and the positive radicle  $\text{CH}_3$  will arrange themselves so as to be as near as possible to each other, and hence the repulsive action of the one and the attractive action of the other will tend to drive the addendum towards position (2) :—



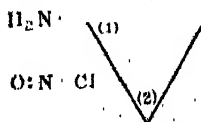
After the final adjustment has taken place, the compound of the opposite configuration is obtained.

In the case of the dibasic acids, such as *L*-aspartic acid, which passes into *L*-malic acid, a similar line of reasoning can be employed. The intermediate compound will be as before.

The repulsive action of the carboxyl groups drives the addendum away from the molecule, and hence any action is confined to position (1) :—

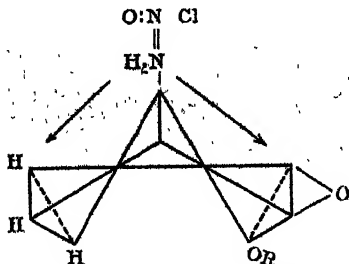


The action of nitrosyl bromide and chloride on the amino acids follows the direction of nitrous acid. It is highly probable that the intermediate compound formed is of the same type :—



The literature dealing with the effect of this reagent is especially interesting, in that the action of both the acids and their esters have been reported upon.

In the case of *D*-alanine ester, which gives rise to *D*- $\alpha$ -bromopropionic ester, the positive ester group takes up a position in opposition to that occupied by the methyl group :—



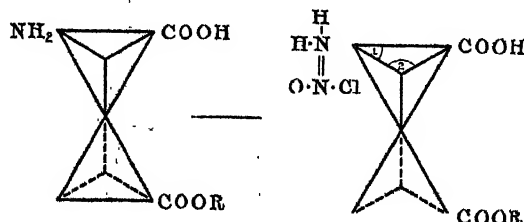
The attractive actions of these positive groups tend to neutralise each other, and hence a simple exchange takes place.

Before considering the amino esters of the dibasic acids the following point must be considered. If the ordinary space configuration be accepted, it follows that there should be two physical isomerides for the mono ester of these substituted acids, according to whether the carboxyl group which is esterified is attached to the same carbon as the substituent or not.

No mention of anything which points to the existence of these isomers can be found in chemical literature, and, although we cannot take their non-existence as proved, it seems probable that there is a favoured arrangement.

The question of the position can be settled by reference to the configuration of the molecule of the acid.

The positive amino group and the negative carboxyl group will cause the upper part of the molecule to be the less reactive on account of the interference, and so the carboxyl attached to the other carbon will be the favoured one.



The positive ester group will attract the addendum, which which be repelled by the carboxyl, and in this way the addendum is drawn towards position (2). After redistribution of the valency and cleavage has taken place, the chlorine is in position (2), and the compound obtained has the opposite sign to its parent.

The above examples are sufficient to give a preliminary statement of a view of the Walden Inversion, which, the writer believes, has not yet received attention.

## INSTITUTE OF INDUSTRY AND COMMERCE.

In order to enable the British public to realise the high standard that has been reached in German industry, and to enable them to appreciate our own shortcomings in that sphere of activity, the Institute of Industry and Commerce has arranged for several articles by prominent men in science and industry to be published on the following subjects :—

- German Methods in Industry.
- First Principles of Production.
- Science and Industry.
- Transportation and Industry.
- Tariffs, Free Trade, and Industry.
- Finance and Industry.
- The State Opportunity and Industry.
- Definition of German Kultur.

The above articles will appear in this journal.

In order that these articles may be appreciated at their proper value the book on British Industry and the War issued by the Institute should be read together with the short thesis written by Sir William Ramsay on "German Methods in Commerce" (CHEMICAL NEWS, cxi., p. 1). These can be obtained from Messrs. Longmans, Green, and Co., Paternoster Row, London, E.C., or from any of the bookstalls of Messrs. W. H. Smith and Sons.

The principal object which the Institute desires to accomplish by the publication of these articles is to create an authoritative work on "National Economics," and by that means to enable the leaders of industry and the public to appreciate what national effort is required to improve the working conditions surrounding British industry.

As Sir William Ramsay has stated, Germany has been conducting two wars, one military and the other industrial; that there has been in existence for some years in Germany a Central Imperial Industrial Council controlling the industrial war on behalf of Germany, and the Institute of Industry and Commerce is intended as an offset to the activities of that organisation in this country.

## PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

Ordinary Meeting, December 17, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the loss the Society had sustained through death on November 28, 1914, of Dr. Johann Wilhelm Hittorf, of Münster, who was elected an Honorary and Foreign Member on February 6, 1908.

It was announced that, in accordance with a decision of the Council, after December, 1914, the *Proceedings* would appear in a contracted form, and would be issued once a month with the Journal.

Messrs. J. D. Robertson, R. R. Baxter, H. M. Spiers, and J. F. Levy were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Samuel Culloch Bone, 30, Long Lane, Garston, Liverpool; Frederick Alfred Mason, B.A., Ph.D., 21, Queen Square, W.C.; Albert Parker, M.Sc., The University, Birmingham; Harold Gordon Rule, B.Sc., Ph.D., 2, Roseneath Terrace, Edinburgh.

The following Certificate has been authorised by the Council for presentation to ballot under By-law I (3):—James Fraser, 44, Cumballa Hill, Bombay, India.

Of the following papers, those marked \* were read:—

\*298. "isoDibenzoylglucosyllose." By FRANK TUTIN.

Power and Salway (*Trans.*, 1914, cv., 767, 1062) described a new, crystalline, bitter substance, dibenzoylglucosyllose, which they obtained from the leaves of *Daviesia latifolia*. The present author now finds that this substance is associated with a small proportion of a more sparingly soluble isomeride, isoDibenzoylglucosyllose,  $C_{27}H_{28}O_{12}$ , crystallises in small, colourless needles, melts at  $173-174^\circ$ , and possesses a bitter taste.

The occurrence of rutin in *Daviesia* leaves has been confirmed.

\*299. "Aromatic Selenium Compounds." (Preliminary Note). By FRANK LEE PYMAN.

Rather more than a year ago, at the suggestion of Dr. Charles Walker, of Glasgow, attempts were made to form the selenium analogue of arsenic acid, namely, *p* aminophenylselenic acid,  $NH_2 \cdot C_6H_4 \cdot SeO_3H$ , in order to determine its physiological action. Whilst aniline sulphate and arsenate readily yield sulphanilic and arsenilic acid respectively at an elevated temperature, no such compound could be obtained from aniline selenate. It was found, however, that phenylselenic acid gave on nitration a *nitrophenylselenic acid*,  $NO_2 \cdot C_6H_4 \cdot SeO_2H$  (yellow needles, m. p.  $156-157^\circ$ ), in good yield. This gave on reduction successively *nitrophenyl diselenide*,  $(NO_2 \cdot C_6H_4 \cdot Se)_2$  (yellow spears, m. p.  $83^\circ$ ), and *amino-phenyl diselenide*, of which the *dihydrochloride* was obtained in a crystalline form,  $(HCl \cdot NH_2 \cdot C_6H_4 \cdot Se)_2$  (yellow grains, m. p.  $291-292^\circ$ ). Aminophenyl diselenide gave on acetylation *acetylaminophenyl diselenide*,  $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot Se)_2$  (yellow needles, m. p.  $185-186^\circ$ ), which dissolved in concentrated nitric acid forming *acetylaminophenylselenic acid*,  $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot SeO_2H$  (colourless needles, m. p.  $209^\circ$ ). From the latter compound the salts of *acetylaminophenylselenic acid* were obtained on oxidation with potassium permanganate, and the free acid was readily hydrolysed with formation of *amino-phenylselenic acid*,  $NH_2 \cdot C_6H_4 \cdot SeO_3H \cdot 2H_2O$  (colourless needles, m. p. of the anhydrous salt  $229^\circ$ ). Whilst it appears probable that these substances are meta-substituted derivatives of aromatic selenium compounds, no direct proof to this end has yet been obtained, but the work will be resumed shortly.

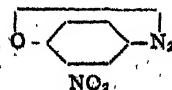
In the meantime it is thought desirable to give a preliminary account of the results obtained in view of the

fact that aromatic selenium compounds are receiving attention from other workers (compare Lesser and Weiss, *Ber.*, 1912, xlv., 1835; 1913, xlv., 2640; Morgan and Elliott, *Proc.*, xxx., 248).

## DISCUSSION.

Professor MORGAN stated that the introduction of selenium into the aromatic nucleus through the agency of the diazo-reaction in conjunction with potassium selenocyanate was applicable only in the case of diazonium compounds which did not yield cyclic diazo-derivatives when their solution was rendered alkaline or even feebly acidic.

For example, the amino-group of *p*-chloroaniline was readily replaced by selenium, but this reaction did not occur with 4-chloro-3-nitroaniline, the diazonium salt of which was converted by alkalis or even by aqueous sodium acetate into the comparatively stable diazo-anhydride—



this product resisting completely the attack of selenocyanate.

Dr. TUCK suggested that it might be possible to settle which nitrophenylselenic acid had been obtained by nitration, by the preparation of the three isomerides by the action of the nitrobenzenediazonium chlorides on potassium selenocyanide. This reaction should give the diselenide which could be converted into the nitrophenylselenic acid by oxidation or into the aminophenylselenic acid by the method described by Dr. Pyman.

\*300. "Blue Adsorption Compounds of Iodine. Part III. Derivatives of 2- and 4-Pyrone." By GEORGE BARGER and WALTER WILLIAM STARLING.

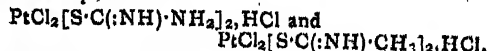
The conditions for the formation of blue additive compounds of iodine with a large number of coumarin, chromone, xanthone, and flavone derivatives were described. These blue substances are sometimes mixed crystals, often amorphous adsorption compounds. The effect of electrolytes on adsorption was discussed, and also the effect of the chemical constitution of the adsorbent.

301. "The Action of Mercuric, Cupric, and Platonic Chlorides on Organic Sulphur Compounds." By PRAFULLA CHANDRA RAY.

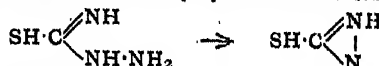
Ethyl and ethylene mercaptans have been found to yield with platonic chloride *chloro-mercaptides* of the formula—

$PtCl(SEt)_2$ ,  $PtCl(SEt)_2$  and  $C_2H_4 \cdot S_2 \cdot PtCl \cdot S \cdot C_2H_4 \cdot SH$  respectively.

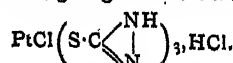
Thiocarbamide and thioacetamide under the action of platonic chloride at first undergo tautomeric change into the stable thiolic modifications,  $NH_2 \cdot C(NH) \cdot SH$  and  $CH_3 \cdot C(NH) \cdot SH$ , respectively, and then react with platonic chloride as in the above typical instances, yielding the *chloro-mercaptides*—



Thiosemicarbazide likewise undergoes tautomeric change, and then loses a molecular proportion of ammonia, thus—



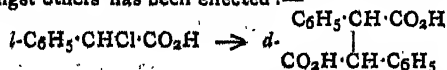
The reactive thiol group in the product is readily attacked by platonic chloride, giving the *chloro-mercaptide*,



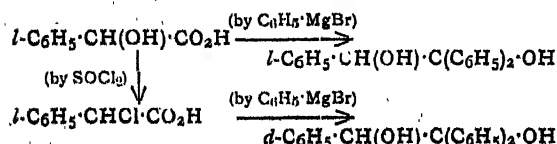
Tautomerisation on exactly similar lines is also brought about by monochloroacetic acid. Similar changes are equally effected by cupric chloride with the formation of

the corresponding cupric chloromercaptides; the latter, however, are not basic, and therefore do not combine with hydrogen chloride. It is found that the behaviour of monochloroacetic acid towards thiocarbamide (*Trans.*, 1914, cv., 2159) and other potential mercaptans is strictly conformable to that of platinic chloride.

302. "Conversion of 1-Phenylchloroacetic Acid into *d*-Diphenylsuccinic Acid," By ALEX. MCKENZIE, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN. The authors have examined the action of certain Grignard reagents on *r*- and *l*-phenylchloroacetic acids and on *r*-phenylbromoacetic acid. The following change amongst others has been effected:—



Both the *d*- and *l*- $\alpha$ , $\beta$ -dihydroxy- $\alpha$ , $\beta$ -3-triphenylethanes can be obtained from *l*-mandelic acid, thus—



303. "A Method of Separating the Dihydroxybenzenes." By THOMAS GRAY and GEORGE SHEVAS CRUIKSHANKS.

Quinol di-*p*-nitrobenzoate is very sparingly soluble in acetone, whereas the corresponding derivative of resorcinol dissolves relatively easily. This property, in conjunction with the sparing solubility of the lead salt of catechol in water, supplies a method for the separation of the three dihydroxybenzenes:

The mixed phenols are dissolved in a small quantity of water, an excess of an aqueous solution of lead acetate is added, and the lead salt of catechol collected. The filtrate is acidified with sulphuric acid, extracted with ether, and the phenols are recovered by evaporating the dried ethereal solution. The residual phenols, consisting substantially of resorcinol and quinol, are then converted into di-*p*-nitrobenzoates, and the latter are separated by crystallisation from acetone. The phenols may be regenerated from the nitrobenzoates by saponification with alcoholic potassium hydroxide in an atmosphere of hydrogen or nitrogen, and subsequent acidification.

*Catechol di-p-nitrobenzoate*,  $\text{C}_{20}\text{H}_{12}\text{O}_8\text{N}_4$ , crystallises from acetone in long, hair-like needles, melting at 154°. One gm. dissolves in 450 cc. of boiling alcohol and in 20 cc. of boiling acetone.

*Resorcinol di-p-nitrobenzoate* forms long, hair-like needles, melting at 182°. One gm. dissolves in 1000 c.c. of boiling alcohol and in 45 cc. of boiling acetone.

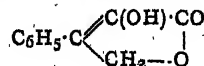
*Quinol di-p-nitrobenzoate* forms needle-shaped crystals or hexagonal plates, melting at 256°. One gm. dissolves in 8000 cc. of boiling alcohol and in 420 cc. of boiling acetone.

304. " $\alpha$ -Hydroxy- $\beta$ -Phenylcrotonolactones." By NORMAN HALL, JAMES EDWARD HYNES, and ARTHUR LAPWORTH.

When an attempt was made to eliminate the oximino-group from  $\alpha$ -oximino- $\beta$ -phenylpropionic acid by heating the latter with formaldehyde and hydrochloric acid, the product obtained was not the expected phenylpyruvic acid,  $\text{C}_9\text{H}_8\text{O}_3$ , but a compound having the formula  $\text{C}_{10}\text{H}_8\text{O}_3$ , derived from phenylpyruvic acid in the following manner— $\text{C}_9\text{H}_8\text{O}_3 + \text{CH}_2\text{O} = \text{C}_{10}\text{H}_8\text{O}_3 + \text{H}_2\text{O}$ .

The new compound is soluble in aqueous sodium carbonate, but is precipitated from the solution by excess of carbon dioxide. It gives an intense green coloration in alcoholic solution with ferric chloride, and, in the same solvent, it instantaneously absorbs at least 0.9 mol. of bromine in the cold. When oxidised with hydrogen peroxide it yields benzoylcarbinol and oxalic acid, whilst on distillation it gives atropic acid and an oil which is probably styrene.

The authors consider that the substance is closely related to the compounds known as "oxolactones," but in view of its behaviour towards bromine and the complete absence of any ketonic characters, they feel confident in ascribing to it the enolic structure—



As the acyl and alkyl derivatives show no ketonic properties they probably also belong to the hydroxycrotonolactone type in spite of the fact that they are inert towards bromine in the cold.

305. "Preparation of Ethyl Malonate and Ethyl Cyanoacetate." By HAROLD ARCHIBALD SCARBOROUGH.

The following process for the preparation of ethyl malonate gives a much better yield than that usually recommended.

In a 1500 cc. flask chloroacetic acid (100 grms.) dissolved in water (200 cc.) is warmed to 50°, neutralised with sodium carbonate, the solution filtered, and then potassium cyanide (80 grms.) is slowly added, the mixture being cooled from time to time so that the reaction does not become violent.

After heating on the water-bath for half-an-hour the flask is connected with a condenser and receiver, and the latter with the pump, and heated on the water-bath under diminished pressure until the whole of the water has been removed and the mass is quite dry. (This is much better than the usual method of removing the water by heating finally at 135°, which always causes decomposition and loss). The almost colourless residue is gradually mixed with a cooled solution of alcohol (200 cc.) and sulphuric acid (160 cc.), and heated on the water-bath for four hours with frequent shaking. Water is then added, the ethyl malonate extracted with ether, the ethereal solution well washed with water and sodium carbonate, dried, the ether distilled off, and the ethyl malonate fractionated under a pressure of 100 mm., and then under ordinary conditions. The yield of the ester boiling at 196°–200° is 104 grms., or 60 per cent of that theoretically possible.

*Preparation of Ethyl Cyanoacetate.*—This ester may be readily prepared by a modification of the process recommended by Kolbe and Hugo Müller (*Annalen*, 1864, cxxxi., 348, 350). Ethyl chloroacetate (100 grms.) dissolved in alcohol (100 cc. of 97 per cent) is mixed with finely powdered potassium cyanide (55 grms.), gradually warmed, and then left until the vigorous reaction has subsided. The mass is then heated to boiling for fifteen minutes, the potassium chloride removed by filtration, and the alcohol removed from the crimson solution by distillation under diminished pressure. The residue is mixed with ether, the ethereal solution filtered, and, after removal of the ether on the water-bath, the crude product is distilled as rapidly as possible under diminished pressure, and then fractionated under ordinary conditions. The yield of ethyl cyanoacetate boiling at 205°–208° is about 45 per cent of that theoretically possible.

306. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XII. The Rotatory Powers of some Esters of Benzoic and of 1- and 2-Naphthoic Acids, with Optically Active Secondary Alcohols." By JOSEPH KENYON and ROBERT HOWSON PICKARD.

A description of the properties of some of the benzoates and 1- and 2-naphthoates of *d*- $\beta$ -butanol, *d*- $\beta$ -hexanol, *d*- $\beta$ -heptanol, *d*- $\beta$ -octanol, *d*- $\beta$ -decanol, *d*- $\beta$ -undecanol, *d*- $\gamma$ -nonanol, and *d*-benzylmethylcarbinol was given. The optical rotatory dispersive powers of the benzoates are simple at low temperatures and complex at higher temperatures, as has been found also in the case of the corresponding aliphatic esters.

On the other hand, the dispersive powers of the naphthoates are complex at low and also at high temperatures in agreement with the hypothesis pre-

viously put forward that the naphthyl radicle and an esterified carboxylic group are each possible centres of a special kind of dynamic isomerism at low and high temperatures respectively.

307. *The Optical Rotatory Power of Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts.* (Part II.). By GEORGE WILLIAM CLOUGH.

The rotatory powers of methyl hydrogen *d*-tartrate, sodium hydrogen *d*-tartrate, methyl *l*-malate, and *l*-malic acid have been measured in aqueous solution and in aqueous sodium chloride at various temperatures. The results of these measurements, together with those recorded in Part I. (*Trans.*, 1914, cv., 49), indicate that sodium and barium haloids in aqueous solution exert a specific effect on the rotatory power of those hydroxy-derivatives of succinic acid which contain a carboxyl or carbalkyloxy-(ester) group, this effect being usually opposite to that caused by dilution.

308. *2:4-Dichlorophenylhydrazine.* By FREDERICK DANIEL CHATTAWAY and CHARLES FREDERICK BYRDE PEARCE.

From the circumstance that 2:4-dichlorophenylhydrazine, which should be obtainable from perhaps the most easily made chloro-substituted aniline, has never been described, it might be inferred that its preparation offers some difficulty. This, however, is not the case; it is easily obtained by the ordinary method, and is a stable, well-crystallised compound showing the usual behaviour of halogen substituted aromatic hydrazines, and yielding a series of well-crystallised hydrazides and hydrazones.

#### SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, January 4, 1915.

Prof. W. R. HODGKINSON in the Chair.

The following paper was read and discussed:—

*"Production of Nitrates from Air, with Special Reference to a New Electric Furnace."* By E. KILBURN SCOTT, A.M.Inst.C.E., M.I.E.E.

This war has emphasised the immense importance of starting the manufacture in this country of nitrates from the atmosphere by electric power. Our enemies have taken care to make themselves independent of Chilean nitrate, for they have several factories producing nitrates from the air.

For several years I have been at work on the problem of evolving a new furnace to work with three-phase alternating current and a system of working a complete plant, with a view to obtaining better yields than are obtained by the present single-phase furnace plants abroad.

The principal points to be met in the design of a furnace are:—

- (1) To ensure that as much of the air as possible is brought into contact with the arc flames.
- (2) To draw off the cool and fixed gas quickly.
- (3) To dispose of the electrodes so as to minimise adjustment and renewals.
- (4) To provide automatic regulation of current and continuity of working.

The author then proceeded to describe and criticise the Birkeland-Eyde, a magnetically-blown Arc Furnace; the Schonherr-Hessberger, a long-standing Arc Furnace; and the Pauling, an air-blown Arc Furnace.

*Importance of Working Three-phase.*—Considering the universality of three-phase apparatus, it is rather surprising that those interested in nitrogen fixation factories abroad should have kept to single-phase designs. When starting to develop a new design of nitrogen fixation furnace, I decided that the proper thing to do was to choose such a method of producing the arc flames that the furnace could be constructed as a self-contained three-phase unit.

*Kilburn Scott Experimental Furnace.*—The three electrodes of the furnace are attached to insulators spaced 120° apart. They are of steel rod  $\frac{1}{2}$  in. diameter, and the inclined sides are bent at about 30° from the vertical line. The rods pass through holes in the wall of the furnace. The bottom ends of the main electrodes are set so as to allow the air to pass freely, and they do not require any adjustment because the pilot sparks always make a path for the main current to get across. The operation of starting up the furnace is very simple. First turn on the air blast, then close the isolating switch so as to make the electrodes alive, and finally close the tumbler switch of the high-frequency set. Directly this is done the sparks jump from the wire to the electrodes, and the three-phase arc flames are started. The top of the furnace (in fact the roof) is a boiler with vertical copper tubes for the gases to pass through. The position of the boiler can be adjusted vertically to obtain the best cooling effect. It is of course connected to earth. As the peak of the arc flame is the neutral point of the three-phase supply it does not matter if it strikes on to the bottom of the boiler. As a matter of fact during the experiments I have frequently placed the boiler so low as to cut off a considerable portion of the upper zone of flame.

*Summary of Advantages of Kilburn Scott Furnace.*—The following may be said to be the special features which distinguish my furnace from those used in Norway and elsewhere. It is essentially a three-phase furnace using the electric energy exactly as generated, and giving three arc flames within one furnace wall. Also for a given periodicity of supply, thrice as many arcs in a given time as would be the case with single-phase. The three-phases give a combined flame of conical shape which is hotter than if the same energy were expended in three separate furnaces, because the latter have only a single flat flame and the radiation losses are much greater. The greater bulk of the three-phase flame also enables more air to come into contact. As compared with three single-phase furnaces, the first cost, the attendance cost, and the maintenance cost are all lower. The space occupied is also much less and there is less brickwork, ironwork, foundations, piping, &c. There are only three electrodes as compared with six for three single-phase furnaces, and this considerably simplifies the electrical and water connections and the renewing of electrodes, &c. Three arcs together help to maintain each other because current is always flowing in one or other of the phases. Thus continuity of working is assured and the load is always balanced. When current is purchased from a power station these are most important matters. By breaking down the air dielectric with high frequency pilot sparks, the arcs start directly the zero points of the alternating current waves are crossed, and this improves the efficiency and power factor. There are no kindling knives to burn away and get in the way of the air supply. The electrodes can be placed at the most suitable distance for the air supply, and do not require any adjustment whatever. The control of a large furnace can be effected by a small tumbler switch on the high-frequency apparatus. The boiler forming the roof of the furnace cools the fixed gas most effectively because of the latent heat of steam, and at the same time the steam so raised can be used to generate electric energy so that the combination can work regeneratively. For a given amount of electric energy the yield of gas may thus be considerably increased.

The concentration of nitric oxide has the highest value at each temperature when the product of oxygen and nitrogen is a maximum. It can be shown that it is directly proportional to the square root of the product thus—Oxygen and nitrogen as in air =  $0.21 \times 0.79 = 0.16$ . Equal parts oxygen and nitrogen  $0.5 \times 0.5 = 0.25$ . Then as—

$$\sqrt{\frac{25}{16}} = \frac{5}{4}$$

The increased yield is, therefore, as 4 is to 5, or 20 per cent.

Since the Notodden factory was first started the percentage concentration of nitric oxide has been double, merely by making small modifications in furnace construction and adjusting the air supply and the electric current. Yet the percentage is still under 20 per cent. The fact that it is so much lower than the theoretically possible is really a most promising feature of the direct method, because it indicates the great scope there is for improvement. A process that is highly efficient from the start is a very tame proposition.

**Gain by regenerative working:** Theoretically the energy saved by using steam from the boiler to generate electricity is about 15 per cent.

**Gain by oxygenated air:** By blowing through the furnace equal parts of oxygen and nitrogen instead of 21 and 79 parts, as they exist in ordinary air, the yield is increased in the ratio of 4 to 5, or by 20 per cent.

**Gain by increased temperature:** The yield increases from 819 to 1850 kg. per k.w. year, or 225 per cent, when the temperature of the arc flames is increased from 3200° C. to 4200° C., or only 30 per cent.

I claim that a combined three phase arc flame is hotter and acts on more of the air than three single-phase flames each in separate furnaces, and that taken in conjunction with the other features of the design detailed above, including the effective cooling by a boiler, using the steam so raised regeneratively, and also blowing oxygenated air through the furnace, a yield considerably in excess of that obtained in Norway is possible.

**Manufacture.**—When considering manufacturing, one naturally thinks first of water power. It is true that such powers as we have are not large, but the assumption that they are not worth harnessing, or if developed electric products cannot be made profitable, is quite untrue. The success of the aluminium works in North Wales and Scotland is evidence of that. No doubt in the future nitrates will be made by electric energy from a water power, but it is not necessary to wait for that. Even if Norway could compete, the establishment of factories in this country to make nitric acid, ammonium nitrate, and sodium nitrate from the air is a national duty. They are urgently wanted for explosives and for the aniline dye industry.

Model furnaces were shown at work and the paper was illustrated with lantern slides and diagrams.

## NOTICES OF BOOKS.

**Technical Methods of Chemical Analysis:** Edited by GEORGE LUNGE, Ph.D., Dr. Ing. English Translation edited by CHARLES ALEXANDER KEANE, D.Sc., Ph.D. Volume III., Part II. London: Gurney and Jackson. 1914.

THE second part of Volume III. of Lunge's compendious work on technical analysis deals with sugar, starch, alcoholic liquors, paper, textile fibres, and inorganic colours. In the section on sugar many additions have been made to the descriptions of the technical analysis of the sugar beet and its products, and those who are interested in the project of the establishment of a British sugar industry will find much valuable information in it. The section on brewing materials and beer has been entirely re-written for the English edition by Messrs. Arthur R. Ling and G. Cecil Jones, and that on inorganic colours, and in fact the whole of the text, has been very thoroughly revised by some of the best known British experts.

**Food Products.** By HENRY C. SHERMAN, Ph.D. New York: The Macmillan Co. 1914.

In this book succinct accounts are given of the composition and food value of the more important classes of foods. The production of each article of food in the United States and elsewhere, and their preparation for

market, are first treated, and many statistics are given. Then the composition and nutritive value are described, and very interesting discussions of the place of each substance in the diet follow. The advice given by the author as to choice of foods, quantities, &c., is based upon sound economic considerations and will be very useful to all who are interested in catering. Copious tables of analysis are included, and much attention is paid to legislation applied to foods, which, although relating chiefly to America, is by no means devoid of interest for English readers.

**London University Guide and University Correspondence College Calendar, 1915.**

THIS guide, which is issued gratis by the University Correspondence College, gives full information relating to the regulations of the examinations of the University to be held in 1915 and 1916, and to the classes of the college. An interesting account is included of the history and constitution of the University, and sound advice is given as to the choice of text-books for the more important examinations.

## CORRESPONDENCE.

### NATIONAL DYE INDUSTRY.

To the Editor of the Chemical News.

SIR,—I have read with very great interest the letter published in to-day's Press by Mr. C. Diamond on the National Dye Scheme. The impression that is left on one's mind after reading the letter, and I do not wish to be unfair to Mr. Diamond, is that the hard-headed business men of Lancashire and Yorkshire are wiser than Mr. Diamond.

The Government Scheme is a palliative, and only forms a part of a very much larger issue. Apart from this consideration it is a most unsound proposal financially.

Business men and the public are asked to subscribe £3,000,000 to establish a National Dye Industry, and the Government will find £1,500,000 on the security of the £3,000,000. There is some wisecracking at the Treasury who knows something. Had the proposition been attractive and had the proper working conditions been there, it would surely have been accomplished long before the declaration of War, but the position of the dye and allied industries is no better off to-day than it was nine months ago.

The whole problem forms part of a very much larger issue. The working conditions which at present surround the whole of our national industries must be considered in their entirety.

At the conclusion of the War we can safely assume that if the working conditions are the same in this country as existed prior to the declaration of War, the German chemical industry will resume the campaign with increased vigour, and should that event happen those who find the three million pounds to establish a National Dye Industry in this country, would realise that what they may now look upon as an investment is in reality a speculation.

The cost of production of articles of utility are continuously on the decrease and never on the increase, even in countries having a protective tariff, and for Mr. Diamond to make the statement that the cost of dyes would be increased to the consumer by the extent of a tariff is to weaken his case. If he had stated that, if a tariff were placed on the raw or natural materials, the consumer of the raw or natural materials would have to pay the tariff, business men would agree with him; but to say that a tariff, if imposed on a manufactured article, would be paid by the consumer is to state a proposition which is not correct. However, history has a good deal to teach us as to the manner in which we have arrived at



our present position, and if any fault is to be found on the historical side it is to be found in the fact that the study of the Science of Production has been left too long with those who are largely engaged in the development of political constitutions. The leading industrialists of to-day are, however, owing to the advance of Science and Education, in a much better position to state precisely the requisite working conditions that are required to produce articles of utility at the lowest possible cost, and incidentally to procure the maximum production of wealth from industry.

The difficulties surrounding the dye industry at the present moment form part of a very much larger issue, which is now being dealt with by the Institute of Industry and Commerce.

The substantial trade and other interests represented by the Institute do not look with favour on the present Government scheme, and consider it very unsound in all its essentials; they, therefore, recommend that, pending the final settlement of the whole of the working conditions which are essential to safeguard our national industries at the conclusion of the War, that no partial settlement of the kind suggested by the Government in the dye industry should be accepted. This is not recommended in any spirit of hostility to the Government; on the contrary, it is recommended in the best interests of British industries as a whole.—I am, &c.,

J. TAYLOR PEDDIE,  
Vice-President and Chairman.

Institute of Industry and Commerce,  
January 11, 1915.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clix, No. 23, December 7, 1914.

**Electrolytic Dissociation of Acetylene and its Metallic Derivatives.**—M. Skossarewsky.—The electrolytic dissociation of acetylene and of its monosodium derivative in solution in liquid ammonia is shown by determinations of conductivity. The dissociation of acetylene increases with the dilution of the solution. The thermic coefficient of the specific conductivity is equal to about 2 per cent per degree, and is almost independent of the concentration. When the mono-sodium derivative of acetylene is electrolysed complex products are obtained, which the author intends to investigate.

**Molecular Transposition in the Cyclohexane Series: Passage to the Cyclopentane Series.**—M. Tiffeneau.—When the iodohydrine of cyclohexane diol is subjected to the action of silver nitrate, cyclopentane carbonic aldehyde is obtained. HI is first eliminated, the cyclic chain opens and then closes on a new carbon, and thus the passage from cyclohexane to pentane is effected. The iodohydrine derived from cyclopentene is transformed by silver nitrate into the corresponding ethylene oxide, no aldehyde being formed.

**Molecular Transposition in the Phenyl Cyclohexane Series: Phenyl Migration without Formation of Cyclopentane.**—Marcel le Brazidec.—In the phenylcyclohexane series the elimination of HI in the iodohydrines of the glycols, effected by the action of silver nitrate, produces only one break between carbons, and the phenyl group migrates from the para- to the meta-position. Thus a true molecular transposition takes place.

**The Sir John Cass Technical Institute.**—The Annual Distribution of Prizes and the opening of the new Metallurgical Laboratory by Sir Robert Mowbray, Bart., the Prime Warden of the Worshipful Company of Goldsmiths, arranged for Wednesday, January 13, has been postponed owing to the death of Sir Owen Roberts, the Chairman of the Governing Body of the Institute.

## MISCELLANEOUS.

**Literary Intelligence.**—As usual, the new issue of the British Pharmacopoeia will be accompanied by the publication of several books which are based upon and supplement the information contained in the official work. In this connection we draw attention to Messrs. J. and A. Churchill's announcements:—"Materia Medica," 14th edition, by Dr. W. Hale White, Physician to Guy's Hospital; "The Book of Prescriptions," 10th edition, by Mr. E. W. Lucas, a member of the B.P. Reference Committee; "The Book of Pharmacopoeias," by Mr. E. W. Lucas and Mr. H. B. Stevens. This is a new book, containing about 5000 formulae, British and foreign, arranged on a comparative system.

## MEETINGS FOR THE WEEK.

MONDAY, 18th.—Royal Society of Arts, 8. (Cantor Lecture). "Oils, their Production and Manufacture," by Dr. F. Mollwo Perkin.

TUESDAY, 19th.—Royal Institution, 3. "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S.

WEDNESDAY, 20th.—Royal Society of Arts, 8. "The Textile Industries of Great Britain and Germany," by J. A. Hunter.

THURSDAY, 21st.—Royal Institution, 3. "Modern Theories and Methods in Medicine," by H. G. Plimmer, F.R.S. Royal Society of Arts, 4.30. "Nepal," by H. J. Elwes, F.R.S.

Institute of Petroleum Technologists, 8. "The Prospects of Oilfields of Western Canada," by E. H. Cunningham Craig.

Royal Society. "Atmospheric Electricity Potential, Gradient at Kew Observatory, 1898-1912," by C. Chree. "Transmission of Electric Waves over the Surface of the Earth," by A. E. H. Love. "Electromagnetic Waves in a Perfectly Conducting Tube," by L. Silberstein. "An Electrically-heated Full Radiator," by H. B. Keeney.

Chemical Society. "Guanidine—Part II, Copper Derivatives," Part III, Potassium Derivatives; Part IV, Silver Derivatives and Constitution," by H. Kral. "Studies on Alcoholysis—Part I, Dilatometric Determination of the Velocity of Alcoholysis in the presence of a Large Excess of Alcohol," by G. K. Kolhatkar. "Wet Oxidation of Metals—Part IV, The Question of Passivity," by B. Lambert. "Velocity of Ionisation at Low Temperatures," by A. R. Normand. "Studies in Catalysis—Part II, The Inversion of Cane-sugar," by A. Langle and W. C. McC. Lewis. "Synthesis of  $\beta$ -Thiol- $\beta$ -phenylethylamine," by H. King. "Nitrites of the Sulphonium Series—Trimethyl and Triethyl Sulphonium Nitrites," by P. C. Ray. "Constitution of the Aminoazo-compounds," by E. C. Baly and R. E. V. Hampson. "The Reactions of both the Ions and the Molecules of Acids, Bases, and Salts—(1) A Re-interpretation of the Reactions of Sodium Methoxide and Sodium Ethoxide with 1,2-Dinitrobenzene, 1,2,4-Dinitrochlorobenzene, and 1,2,4-Dinitrobenzene," by S. F. Acree; (2) "The Reactions of Sodium Ethoxide with Methyl Iodide in Absolute Ethyl Alcohol at 25°," by H. C. Robertson and S. F. Acree; (3) "The Conductivity and Ionisation of Sodium Ethoxide, Potassium Ethoxide, Lithium Ethoxide, Sodium Phenoxide, Potassium Phenoxide, Lithium Phenoxide, Sodium Phenolthioureaol, Sodium Iodide, Sodium Bromide, and Mixtures of these Electrolytes in Absolute Ethyl Alcohol at 0°, 25°, and 35°," by H. C. Robertson and S. F. Acree; (4) "The Reaction of Sodium Ethoxide with Ethyl Bromide and Ethyl Iodide in Absolute Ethyl Alcohol at 25°," by E. K. Marshall and S. F. Acree. "Addition of Auxochromes in the Flavone Group," by A. G. Perkin and E. R. Watson.

FRIDAY, 22nd.—Royal Institution, 9. "Problems of Hydrogen and the Rare Gases," by Sir James Dewar, F.R.S., &c. Physical, 5. "Practical Harmonic Analysis," by A. Russell. "Measuring the Focal Length of a Photographic Lens," by T. Smith.

SATURDAY, 23rd.—Royal Institution, 3. "Aerial Navigation—Scientific Principles," by R. T. Glazebrook, C.B., F.R.S., &c.

## THE CHEMICAL NEWS.

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## SPERMACETI:

## ITS SOLIDIFYING AND MELTING POINT.

By ROBERT MELDRUM.

THE following investigation was undertaken with the view of obtaining a better understanding of the solidifying and melting point, their relation and co-relationship. Spermaceti was selected as being of a highly crystalline nature, the absence of a "rise" on setting, and being free from free fatty acids and glycerides. Of all the fats, waxes, and fatty acids spermaceti is one of the most highly crystallised, and is therefore important as regards investigating the phenomena of the "rise" which takes place in solidifying, and also the "zero" point. It is well known erratic phenomena is present during the determination of the melting and solidifying point of nearly all fats and waxes which is not clearly understood. With the view of attempting to determine the conditions which govern these fixed points, the author undertook the following investigation. A 50° C. mercury thermometer was used, divided into 1/10ths.

*The Solidifying Point.*

**By Dulican's Method.**—The following five determinations were made by this well-known method. The test-tube used was 7" x 1", half filled with melted wax, and melted at 20° C. above melting point. The tube fixed in apparatus, and when crystals appeared at bottom stirred thrice to left and thrice to right, and then fixed thermometer in centre 1" from bottom.

Solidifying point, °C.	45.75	45.75	45.75	45.75	45.75
Rise (less than), °C.	0.05	0.05	0.05	0.05	0.05
Time ther. stationary, min.	10	10	10	10	10

The spermaceti, melted at 100° C. for two hours and six hours, repeatedly melted and re-melted at that temperature, rapidly cooled and slowly cooled, gave the same results as above, thus showing the solidifying point to be unaffected by such thermal treatment. It is remarkable that spermaceti, with its pronounced crystalline structure, yields so small a "rise," whereas some waxes, weakly crystalline, will yield as much as 10° C. It would therefore appear that there is no relation between crystalline structure and the "rise."

**Effect of Rapid Cooling.**—By plunging the tube into cold water when the molten wax is at 46° C., the solidifying point is apparently reduced 0.2° C., though theory demands that rapid cooling ought to give a result higher than 45.75° C., or cause a higher "rise," as the speed of crystallisation is greater. So far as spermaceti is concerned, increased speed of crystallisation lowers the solidifying point, as will be seen from results:—

Solidifying point, °C.	45.55	45.55	45.55	45.65
Rise (less than), °C.	0.05	0.05	0.05	0.05
Therm. stationary, min.	3	5	4	5

**Effect of Slow Cooling.**—Melted wax at 60° C. and cooled by stirring to 46° C. Placed tube in water jacket at 44° C., and maintained water jacket at this temperature till solidification was complete. It will be evident that if molten wax is at 45.7° C. and water jacket at 45.7° C., and both equally maintained at this temperature, the time during which the thermometer would remain stationary

would be unlimited; but the temperature of water jacket being 1.7° C. lower than solidifying point, allows the stationary point to be observed within a reasonable time. Theory demands a higher "rise" or higher solidifying point, which actually takes place.

Solidifying point + rise, °C.	45.75	45.95	45.85
Rise (less than), °C.	0.05	0.05	0.05
Time therm. stationary, min.	40	40	40

**Effect of Stirring while Solidifying.**—The phenomena which takes place here is generally applicable to all fats and wax. While stirring at the beginning and during solidification, and continuing till thick and semi-solid, on ceasing stirring through all these stages the thermometer rises.

While stirring, thermometer remains at 45.6° C.  
On ceasing to stir, thermometer rises to 45.75° C.

**Effect of Tube Diameter.**—The diameter tube has no influence on the solidifying point. Experiments made with tube from 1/4" to 3/4" diameter yield the same results. The following are the results obtained with tubes 3/4" diameter:—

Solidifying point + rise, °C.	45.75	45.75	45.75
Rise (less than), °C.	0.05	0.05	0.05
Therm. stationary, min.	1	0	5
Minutes to fall 0.2° C. below solidifying point	4	2	3

Even with these small-bore tubes the point of solidification may be accurately determined by timing the fall of the thermometer 0.1° C. or 0.2° C. from maximum rise; unless this is done the stationary point is rather indefinite.

**The Stationary Point.**—The point at which the thermometer remains stationary for the longest period is the declared solidifying point; as it is this point which can most accurately and definitely be determined. The phenomena of the stationary point is due to layers of solid fat forming on walls of tube, which act as a non-conductor, and which increase in thickness per unit of time, reducing the mass of molten wax, and when thickness of non-conducting walls are at maximum and molten wax at minimum the thermometer commences to fall. Spermaceti was melted in test-tube 7" x 1" and cooled by stirring to 46° C., thermometer fixed in centre, and placed in solidifying apparatus. Four minutes after thermometer had remained stationary the tube was examined internally. All was liquid in centre, there being about 1/4" solid wax on walls. Another similar tube, but allowed to solidify at 45.7° C. and then allowed to fall to 45.5° C., when examined was all solid hard wax, with a little liquid in centre, the wax having shrunk away from thermometer. It would therefore appear that the speed of crystallising, change in viscosity of melt, or rapid changes in density take no part in determining the point of solidification. The temperature to which the thermometer falls and remains stationary is apparently determined by the increased non-conductivity of the walls of tube by solidified layers of wax.

**The Critical Point.**—The author has determined this point with the view of ascertaining the point at which solidification commences and liquefaction ends. The point at which opacity commences on cooling and ceases on heating has been determined in tubes 7" x 1", half filled with the wax, immersed in a large hot-water jacket.

*No. 1 Experiment.*

Spermaceti melted, and allowed to solidify in tube till temperature fell to 40° C. Placed in apparatus, and heated at rate of 0.25° C. per minute during the stirring of jacket. Placed thermometer in centre of tube, and stirred when sufficiently fluid.

- 44.5 Pasty soft solid; opaque  
 45.0 Pasty semi-liquid; opaque.  
 45.3 Thick opaque liquid.  
 45.5 Opaque thin liquid.  
 45.7 Opaque fluid liquid; five minutes not clear.  
 46.2 Slightly opaque limpid liquid; five minutes.  
 46.4 Transparent limpid liquid; opacity gone.  
 45.8 Opacity reappears by floating scales and flocculent grains. Gains opacity rapidly when temperature maintained. Rises to 45.9° C., and then falls quickly.  
 45.7 Thick opaque liquid; can be stirred.  
 45.6 Thick opaque liquid; drips from thermometer; solidifies round walls of tube.  
 45.5 Pasty solid inside tube; hard round walls.

*No. 2 Experiment.*

Temperature maintained five minutes at each period.

Wax, °C. Water jacket, °C.

- 49 49.1 } No opacity or floating scales.  
 47 47.2 }  
 46.5 46.4 Cloudy matter descends from top of fat which re-dissolves on stirring.  
 46.0 46.2 Scales appear rising from top and bottom.  
 45.9 45.7 Very opaque. Full of scales.  
 46.1 46.2 Still opaque. Not all melted.  
 46.5 46.9 Transparent. All melted.

*No. 3 Experiment.*

Wax in tube, 46.5° C.; water jacket, 46.5° C.; maintained for ten minutes. Cloudy matter descends from surface of molten wax, which dissolves on stirring. No indication of setting. No opacity.

*No. 4 Experiment.*

Wax in tube, 46° C.; water jacket, 46° C.; maintained temperatures for twenty minutes, both stirred. Cloudy matter descends from top, which re-dissolves on stirring. No opacity. No indications of setting.

Wax in tube, 45.9° C.; water jacket, 45.7° C.; temperatures maintained five minutes. Both stirred. Cloudiness comes from top, which does not re-dissolve on stirring. Wax very fluid and slightly cloudy.

Wax in tube, 45.8° C.; water jacket, 44.8° C.; five minutes. Becomes opaque, full of scales; setting distinctly commences.

Wax in tube, 46.4° C.; water jacket, 46.5° C.; completely transparent. No floating scales.

The above four experiments show that solidification commences by determining the opacity point between 45.8–45.9° C.; a very close agreement with the ordinary method. The melting point, as determined by this method in Experiment 4, is 46° C. This method of determining melting and solidifying points has much to recommend it, as both points are very definite, and the test is made under good conditions, that is a fine suspension of solid wax in molten wax at the determined temperature; in addition to a water jacket maintained at nearly the same temperature as the molten wax.

*Melting Point.**Thermometer Bulb Method.*

- Drop appears, °C. .. 45.3 45.3 45.3 45.5  
 Drops off, °C. .. 45.6 45.6 45.6 46.3

*Open Capillary Tube Method.*

- Wax rises at °C. 45.3 45.4 45.1 45.3 45.2

*Closed Capillary Tube Method.*

- Melting point, °C. .. 45.9 46.0 45.9  
 Solidifying point, °C. .. 45.0 44.8 44.7

The most interesting features of these determinations is that by the thermometer bulb method and open capillary tube method the melting points are lower than the actual solidifying point. This again shows the presence of erratic phenomena which modifies the melting point determination, and which is the cause of so much perplexity in innumerable published results. It must be apparent that the melting point must be higher than the solidifying point.

*Summary.*

	Lowest °C.	Highest °C.
Solidifying point by Dalican's method ..	45.75	45.75
Solidifying point in small bore tube ..	45.75	45.75
Solidifying point by slow cooling ..	45.75	45.93
Solidifying point by stirring ..	45.75	—
Solidifying point, opacity method ..	45.8	46.0
Solidifying point, capillary tube ..	44.7	45.0
Melting point, thermometer bulb method ..	45.3	45.5
Melting point, open capillary tube ..	45.1	45.4
Melting point, closed capillary tube ..	45.9	46.0
Melting point, opacity method ..	46.0	46.4

*Influence of Impurities.*

0.1 per cent water, glycerin, does not lower or raise the solidifying point or affect the "rise." 0.1 per cent oleic acid has no effect. It is generally understood that the presence of moisture, free glycerin, and free fatty acids in small proportion modify the solidifying point and yield erratic results, but the author has found this not to be so.

*Cooling Ratios.*

The cooling ratios are very useful in confirming the solidifying point, when that point is not well defined, due to a rapid fall in the thermometer. Especially is this so with the solid glycerides where the thermometer rapidly rises and falls between the "zero" point and solidifying point. In these cases the author has been in the habit of locating the solidifying point by determining the cooling ratios. The cooling ratios for spermaceti in a tube 1½ ins. diameter, half full, is as follows:—

°C.	Seconds.	°C.	Seconds.
48 to 47.5	30	48 to 47..	60
47.5 to 47.0	30	—	—
47.0 to 46.5	60	47 to 46 ..	150
46.5 to 46.0	90	—	—
46.0 to 45.85	180	46 to 45.85 ..	180
45.85 to 45.7	1080	45.85 to 45.7 ..	1120
45.7 to 45.5	720	45.70 to 45.5 ..	480

*Influence of Sperm Oil.*

As both the melting and solidification are used to determine the purity of innumerable substances, it was considered advisable to investigate the effects of sperm oil in lowering the solidifying point and melting point and how far the "rise" was affected. Repeated melting and cooling, and heating for long periods considerably in excess of the melting point, was found to have no effect on the results. This confirms the former results obtained by the author in similar experiments with fatty acids and the solid glycerides.

*80 per cent Spermaceti + 20 per cent Sperm Oil.*

- Solidifying point + rise, °C. .. 44.1 44.1 44.1 44.1  
 Rise less than °C. .. 0.05 0.05 0.05 0.05  
 Minutes thermometer stationary .. 7 7 7 7

Thermometer falls from 45 to 44.6° in one minute; from 44 to 42 in nine minutes. No observed "zero" or stationary point while solidified in cold water, but thermometer falls slowly. Solidifies at 44.2° in hot water jacket. Wax melted at 70° C., and cooled by stirring to 46° C., and placed in hot water at 46° C. no trace solidification in five minutes from 45.5 to 44.4° C.; at 44.2° C. solidification commences. Melting point by opacity

method, 44.8° C. It will be noted that 20 per cent sperm oil only lowers the solidifying point by 1.65° C. or 0.08° per cent oil. Such a large percentage of oil in spermaceti could easily be detected by a visible examination of same, and it would not be necessary to apply melting point methods. But with 5 per cent oil present, the thermometer would only be about 0.2° C. below normal. This strongly points to the fact that in melting point and solidification methods for either analytical or scientific purposes, the thermometers used must be absolutely accurate, and the degrees divided into at least 0.05° or less, as it is only by observing very small variations in the solidifying and melting point below or above normal that the purity of a substance can be determined.

95 per cent Sperm Oil + 5 per cent Spermaceti.

No solidifying point observed when allowed to cool to 14.5°. By the opacity method, solidifying point 23° and melting point 26.5°.

90 per cent Sperm Oil + 10 per cent Spermaceti.

No solidifying point observed when cooled to 22° C. By opacity method, solidifying point 28.1°, 28.1°, and melting point 31.5°, 30.3°.

At these extreme dilutions the stationary point vanishes, and explains the erratic results obtained in determining low melting mixtures.

## ESTIMATION OF SULPHUR IN MOTOR SPIRITS.

(SECOND COMMUNICATION).

By W. A. BRADBURY and F. OWEN.

OUR first communication on this subject appeared in the CHEMICAL NEWS of October 2, 1914. We have continued our experiments, and have so perfected the method that we are now able to make the estimation by a volumetric method in about two hours. The modified apparatus is shown in the sketch. The combustion chamber is a litre Jena flask with a round bottom. The neck is cut off and so shortened that the burner of the carburettor just enters the flask. On the end of the neck is fitted a tinned copper disc, 2½ inches diameter, perforated round its circumference with small holes; on the bottom of the disc, on the outside edge, a narrow ring is soldered; on the top of the disc a deeper ring is soldered, and the space between the neck and the ring is fitted with a cork. The glass absorbing vessel is just large enough in diameter to allow the copper disc to enter easily. The lower ring of the copper disc rests on the narrowing portion of the absorbing vessel, and forms a cup-like arrangement which catches the gases of combustion and forces them to pass through the perforations of the disc and through the absorbing liquid. On the carburettor we have substituted mercury cups for the indiarubber connections, thus reducing very considerably the liability to damage.

The method of working is as follows:—10 cc. of the spirit to be tested is run by means of a pipette into the carburettor c; the auxiliary carburettor c contains pure benzene. Into the absorption vessel is placed 50 cc. of a standard solution of sodium carbonate (about N/10) and 20 cc. of ordinary neutral peroxide of hydrogen (10 vol.).

We will now re-describe the method of burning off the spirit. The air required for the combustion is obtained by means of a water blower, and connected up to the carburettors. The blower is started and the clip x is opened, and air blown through the benzene in the auxiliary carburettor; the gas formed is lighted at v; clip z is gradually opened and extra air mixed with the gas until a good blue flame is obtained, but not a large flame. The combustion chamber (flask) is now gradually lowered over the flame until the disc is covered by the absorbing liquid and the

gases are bubbling through. Air is now turned through the spirit to be tested by opening clip 3, and the auxiliary gradually turned off by closing clip 1. The proper regulation of the various clips must be left to the skill of the experimenter to obtain a small clear blue flame and the platinum coil above the gauze cap of the burner at its maximum state of incandescence, and it must be kept at this throughout the experiment. As soon as the experiment is proceeding satisfactorily (and the operations are really very easy), the water-bath is filled with water at 80° F., and then very gradually heated through the experiment, so that the temperature at the end of the experiment is about 110–120° F. When only about 1 cc. of the spirit is unburnt about 1 cc. of absolute alcohol is run into the carburettor by the tube above clip 4; two washings with alcohol in this manner are sufficient to clear the carburettor of the spirit being tested. When this has been effected the air supply is reduced, and the air allowed to bubble through the liquid very gently until the chamber is cold. The chamber is then washed out with water into a beaker, the contents of the absorbing vessel are emptied into the beaker, and the vessel washed out; the contents of the beaker are then raised to boiling-point, to get rid of oxygen and carbonic acid; lacmoid is then added, and the excess sodium carbonate determined by standard sulphuric acid (1 cc. = 0.0343 BaSO<sub>4</sub> or 0.00471 sulphur).

10 cc. Benzene taken.

50 cc. Na<sub>2</sub>CO<sub>3</sub> required 17.8 cc. standard acid.

Excess Na<sub>2</sub>CO<sub>3</sub> = 6.2 cc. standard acid.

Na<sub>2</sub>CO<sub>3</sub> neutralised = 11.6 cc. standard acid.

Combustion of benzene = 11.6 cc. standard acid.

Grms. per litre × 70 = grains per gallon.

∴ 11.6 × 0.00471 × 100 × 70 = 382 grs. of sulphur per gallon.

The following results show the value of the method:—

Substance tested.	Method.	Result.
(1) CS <sub>2</sub> in benzene	Volumetric	98.7 p.c. of theoretical
Benzole	(a) Gravimetric	395 grains per gallon
Benzole	Volumetric	398 " "
Benzole	Volumetric	395 " "
(2) Benzole	(b) Gravimetric	296 " "
Benzole	Volumetric	305 " "
(3) Benzole	(c) Gravimetric	240 " "
Benzole	(d) Gravimetric	248 " "
(4) Benzole	Volumetric	383 " "
Benzole	Volumetric	378 " "
Benzole	Volumetric	378 " "
Benzole	Volumetric	374 " "

The tests a, b, c were done with the bead-tube apparatus, described in our first communication; the sample d in the volumetric apparatus.

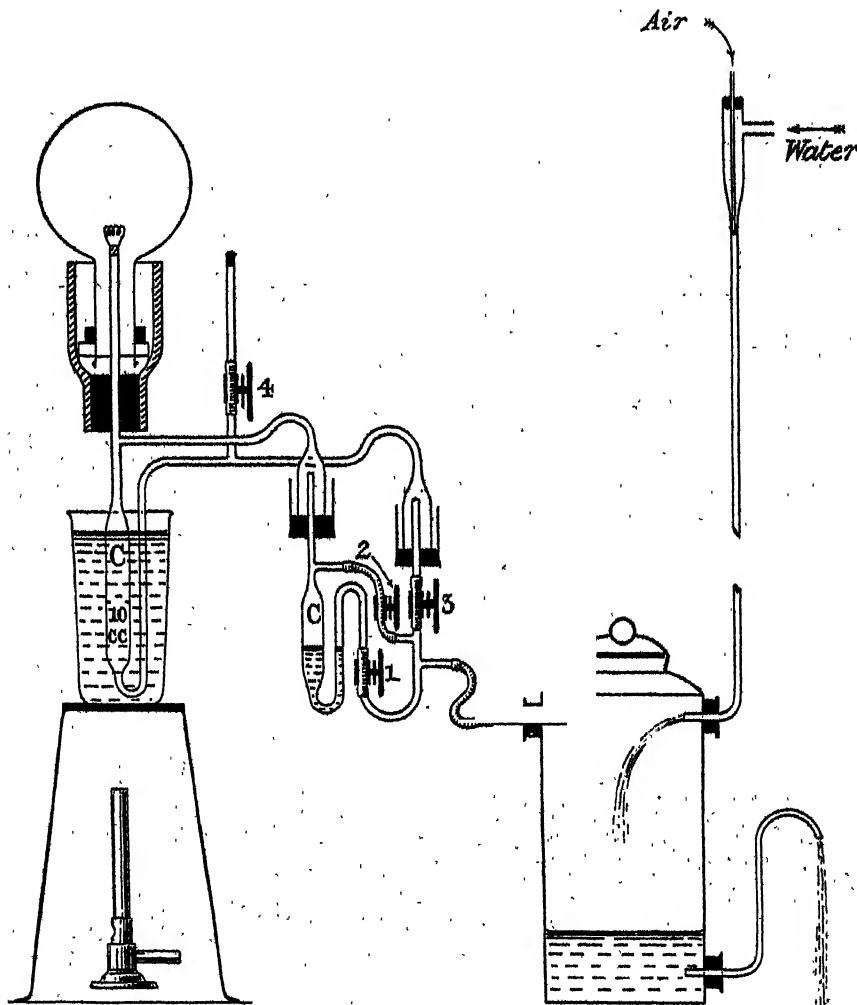
Other workers, using a wick lamp, have evidently found the absorption of the products of combustion to be an uncertain factor, as the number of absorption flasks has varied considerably, and as many as ten flasks have been used.

The apparatus which we now use has brought the absorption problem to its simplest form; the results of our experiments prove that the absorption can be effected in one vessel. This is no doubt due to having to deal only with the products of combustion, whereas when a wick-lamp is used and the combustion takes place in an open-mouthed tube and an aspirator is required to draw the products through the flasks, a large amount of excess air is also drawn through.

The ease with which we can now estimate the sulphur in motor spirits has induced us to test the following points:—In all our experiments we have completely burnt off all the spirit to be tested; it has, however, been re-

## Results of Burning Benzole in a Spirit-lamp in Stages.

	1.	2.	3.	4.	5.	6.	7.	8.
Benzole in lamp .. .. .	200	175	150	125	100	75	50	25
Sulphur in grains per gallon .. .. .	383	295	285	338	357	424	424	383
Total sulphur in lamp .. .. .	76600	51625	42750	42250	35700	31800	21200	9575
Sulphur withdrawn for test .. .. .	1915	1475	1425	1690	1785	2120	5300	
Sulphur in lamp after withdrawal of test .. .. .	74685	50150	41325	40560	33915	29680	15900	
Sulphur in lamp after burning down to mark .. .. .	51625	42750	42250	35700	31800	21200	9575	
Sulphur burnt by burning down to mark .. .. .	23060	7400	925	4860	2115	8180	6225	
Grains of sulphur per gallon in burnt portion .. .. .	1153	370	0	243	106	44	316	



commended in several methods to weigh the lamp before and after burning, to ascertain the quantity of spirit burnt. Apparently it was taken for granted that the spirit burns as an homogeneous substance. On the other hand, two opposite statements have also been made. Firstly, that all the sulphur is burnt off with the first portion of the spirit; and, secondly, that the sulphur is burnt off with the last portion of the spirit, and causes the flame to smoke unless the wick is very low.

To test these points we made the following experiments:—A spirit lamp was graduated into eight parts of 25 cc. each; 200 cc. of benzole were filled into the lamp,

5 cc. were pipetted out, and the sulphur estimated. The lamp was then lighted and the spirit burnt down to the first mark, *i.e.*, 20 cc. were burnt; 5 cc. of the residue were taken out and the sulphur estimated, the lamp re-lighted, and the spirit burnt down to the second mark. These operations were repeated until 25 cc. were left; 5 cc. were tested for the estimation of the sulphur left in the lamp.

The following table gives a summary of the results obtained. The method of calculating the results is as follows (cc.'s are assumed to be gallons for purposes of calculation):—

200 taken containing 383 gra. per gallon = 76,600 gra.  
5 taken for test, containing 383 gra. per  
gallon .. .. . = 1,915 "

195 left in lamp contain .. .. . 74,685 "

20 burnt.

175 left after first burning, containing  
295 gra. .. .. . 51,625 "

Hence the 20 burnt contained .. .. . 23,060 "

Or at the rate of 1153 gra. per gallon.

175 left after first burning and containing  
295 gra. per gallon .. .. . = 51,625 "

5 taken for test and containing 295 gra.  
per gallon .. .. . = 1,475 "

170 left in lamp contain .. .. . 50,150 "

20 burnt.

150 left after second burning and con-  
taining 285 gra. per gallon .. .. 42,750 "

Hence 20 burnt contains .. .. . 7,400 "

Or at the rate of 370 gra. per gallon.

Sample.	Sulphur in lamp before burning.	Sulphur burnt.	Per cent of the sulphur in lamp before burning.	Per cent of sulphur in original quan- tity taken.	Sulphur with- drawn for tests.
1.	74,685	23,060	30.80	30.10	1915
2.	50,150	7,400	14.75	9.66	1475
3.	41,325	—	—	—	1425
4.	49,560	4,860	12.00	6.34	1690
5.	33,915	2,115	6.24	2.76	1785
6.	29,680	8,480	28.60	11.07	2120
7.	15,900	6,325	39.00	8.26	5300
		52,240			15,710
				Per cent.	
				52,240 = 68.10	
				15,710 = 20.50	
				9,575 = 12.50	
				Total .. .. . 77,525	101.10
				On original portion .. .. . 76,600	
				Error in excess .. .. . 925 = 1.1	

These results show that for this particular sample of benzole all the statements respecting the burning of the sulphur are erroneous, and that correct estimations of the sulphur can only be obtained by completely burning all the spirit. They also show that a selective action does occur, and from the varying amounts of sulphur per gallon for the spirit burnt it seems justifiable to conclude that the sulphur occurs in different combinations.

To test whether an unlighted wick has this selective property, 75 cc. of benzole were filled into a spirit lamp, and about one inch of the wick was drawn through the burner and left exposed to the atmosphere until 25 cc. of the benzole had evaporated.

The original benzole contained 383 grains sulphur per gallon.

The benzole left in the lamp, 383 grains sulphur per gallon.

∴ The benzole evaporated also contained 383 grains sulphur per gallon.

75 at 383 = 28,725  
50 at 383 = 19,150

Lost in 25.. 9,575  
∴ x contains 383

No selective action has occurred in this case.

In our first communication we showed that concordant results could not be obtained by burning motor spirit from a wick lamp, and that the errors were due to imperfect combustion; and although we have abandoned this method of burning, the experiments are interesting as showing the selective action of a wick lamp burning benzole.

The following gives the tests from an ordinary distillation. The sample contained 348 grains per gallon. 100 cc. benzole distilled and 5 fractions obtained.

100 containing 348 gra. per gallon ..	= 34800
First drop at 173° F.	
20 cc. up to 180° F. 854 gra. per gall.	17080 = 49.1
20 cc. " 186° F. 246 "	4920 = 14.1
20 cc. " 198° F. 139 "	2780 = 8.0
20 cc. " 206° F. 172 "	3440 = 9.8
20 cc. " 247° F. 139 "	2780 = 8.0
100	31000 89.0

Lost in fractions, 11 per cent.

49 per cent of the sulphur is contained in the first fraction of 20 per cent.

## CHEMISTRY AND INDUSTRY.\*

By Sir W. GEORGE WATSON, Bart., Chairman of Maypole Dairy Co., Ltd.

THE Great War has demonstrated the disadvantages of Great Britain being too dependent upon any foreign country for the preparation of its supplies of food or essential articles like aniline dyes, glass, leather, and other necessities for some of the large British industries.

The research and painstaking work of the University-educated chemical engineers, so generally employed by German manufacturers, has resulted in the discovery of new processes, technical knowledge, and experience, which are of course unknown in this country.

The Government have recently established the principle of giving a "development grant," but our politicians might recognise that the only real difference between a "tariff" and a "development grant," or loan, is that in the one case the public pay the initial cost (if any) of assisting the transfer of a new industry to the country, and in the other case the cost is paid by the taxpayer—which is only another name for the public.

Manufacturers of all nationalities will generally concentrate on those manufactures which pay them best. If a manufacturer, with works in Germany, and doing a large British trade, found that he could secure a "development grant" or escape a "tariff" by erecting works in England, he would probably do it; but in the absence of this special inducement he will continue to supply the British demand from the German factory, as he then saves the extra expense of running two factories and separate managements, and he has also less risk of the discovery, by his competitors, of the secret processes, &c., which are the result of the research work of his chemical engineers.

The present war may have the effect of bringing some German industries to the United Kingdom, but it is still more likely to assist in transferring to neutral countries those German industries which have formerly largely supplied the British market. Manufacturers in neutral countries can, even in time of war, import the special German machinery, and possibly get the German personnel, with the necessary experience and knowledge, whereas this course is quite impossible for the British manufacturer.



The British public are too prone to think that, given the necessary capital and labour, it is possible to profitably and successfully manufacture in the United Kingdom anything which may be in demand. They forget that the necessary special machinery or technical and scientific knowledge may be unobtainable, as Continental manufacturers who keep large research staffs of chemical engineers often prefer to keep their new processes secret instead of patenting them, and thereby publishing them to the world at large.

A good illustration of the points herein raised can be given by the margarine trade, of which I can speak with considerable knowledge.

Originally the margarine consumed in Germany, Belgium, and England was all made in Holland, but when the trade became important the German and Belgian Governments put on a tariff which promptly caused the chief Dutch makers (often with the assistance of English capital) to build works to enable them to manufacture margarine in Germany and Belgium, whereas they have not built works in England, and they still continue to supply their English customers from their factories in Holland.

Previous to the outbreak of war the raw materials used in the Dutch and German factories largely came from British Colonies, and consisted of nuts and seeds, which were generally crushed and refined in Germany, thanks to the skill of the German chemical engineers. From Germany much of the refined oil required for the Dutch margarine factories was transferred to Holland, which, in some cases, only meant a short journey down a river from the German oil mill and refinery to the Dutch margarine works, often under the same ownership.

The nuts and seeds are chiefly produced in the British Colonies, and in consequence of the war and the shortage of refining plants and skilled chemical knowledge of refinery in England, the price of same has, since the outbreak of war, fallen £2 per ton, whereas the price of refined coconut and palm kernel oil has at same time advanced £25 per ton. The nut-producing British Colonies are suffering from lack of demand, and from the low prices now obtainable for their nuts, and the British public have to pay higher prices for their margarine.

I think these facts, and the present and very similar conditions respecting sugar, leather, and aniline dyes, &c., proves the necessity of a policy calculated to make the British Empire more self-supporting as regards supplies of essential articles. Whether this is done by means of tariffs or by means of development grants or loans is quite unimportant to those who can look at the matter solely from an Imperial and business point of view, and apart from all questions of politics.

I understand that the British Government propose to offer a large loan to the aniline dye industry. Now that chemistry is the basis of so many of our manufacturing industries, the principals of our public schools and universities should recognise that the teaching of modern languages and the teaching and training of chemical engineers is equally as useful as the study of Latin and Greek. The students in later life will certainly find it more profitable.

In this respect the report on German trade for the year 1913 by Sir Francis Oppenheimer, His Majesty's Commercial Attaché in Germany, is worth studying. On page 60 of the report he makes the following observation with regard to the chemical industry in Germany—namely, "The prosperity of the German chemical industry is notorious. It yields higher profits than any other industry as a whole." Various statistics follow which fully confirm this observation, and coming from such an authentic source should remove any doubt which may linger in our minds as to the need for re-establishing this industry in all its branches in Great Britain. It is an additional reason why Great Britain must not be dependent upon any foreign country for the supply of its essential materials.

## THE ATOMIC WEIGHT OF LEAD OF RADIO-ACTIVE ORIGIN.\*

By THEODORE W. RICHARDS and MAX E. LEMBERT.

It has been pointed out by many of the workers upon radio-activity, especially by Boltwood, Ramsay, Rutherford, and Fajans, that the most conclusive test concerning the recent theory of the degeneration of radio-active elements is to be found in the determination of the atomic weights. If each  $\alpha$ -transformation involves the loss of an atom of helium and nothing else which is weighable, the atomic weight of the product should be just 3.99 less than that of the original substance, because 3.99 is the atomic weight of helium evolved during the  $\alpha$ -transformation. Thus, if radium has an atomic weight of 225.97 (Königschmid, *Moskowsk*, 1912, xxxiii., 253), its emanation ("niton") should have an atomic weight of 221.98, radium D (which is supposed to involve three more  $\alpha$  transformations) should be 210.01; and radium G (yet another  $\alpha$ -transformation) should be 206.02.

Still more recently a further theory, which has been independently proposed by Fajans (*Ber.*, 1913, xli., 422), and by Soddy (*Chem. News*, 1913, cvii., 97, see "The Chemistry of the Radio-elements," 1914, ii., 3), indicates that some of the places in the periodic table corresponding to high atomic weights, should, perhaps, include several elements, different in atomic weight but very similar in other properties. Thus, in the place which we usually assign to lead, we should expect to find a mixture of ordinary lead, radium B, D, and G; and, perhaps, also at least one other radio-active product from thorium and one from actinium. These different substances, according to the hypothesis, should have identical spectra and be inseparable by chemical means, but, coming from different sources, they should have different atomic weights. The theory supposes that each  $\alpha$ -transformation involves a loss of valence of two, and each  $\beta$ -transformation a gain of valence of one. The  $\beta$ -transformation involves no change of weight. Thus, radium D (supposed to have an atomic weight of 210), after two  $\beta$  and one  $\alpha$  transformations, returns again as radium G to the same place in the periodic system with an atomic weight of only 206. This place is that assigned to lead (which some suppose to be primarily radium G), the only one of the radium series possessed of a long life and not highly radio-active.

The problem is one capable of a decisive gravimetric test; specimens of lead, consisting of different mixtures, obtained from different sources, should have different atomic weights. On the generous suggestion of Dr. Fajans this matter was taken up in the autumn of 1913 at Harvard.

(NOTE.—Mr. Max E. Lemberg, Dipl. Ing., a pupil of Dr. Fajans, was sent by him and the Technische Hochschule, of Karlsruhe, with the support of Prof. Bredig, to Harvard University especially for this purpose. Sir William Ramsay, also, at about the same time had urged on behalf of Dr. Soddy that the atomic weight of radio-active lead should be studied in the Wolcott Gibbs Memorial Laboratory. It is needless to say that the opportunity was welcomed; indeed, the matter would have been taken up here before, except for a fear of trespassing upon a field which might properly be considered as belonging to the proposers of the theory. A brief announcement of this work was made by Dr. Fajans at the meeting of the Bunsen Gesellschaft in Leipzig on May 21, and a brief notice was published in *Science* on June 5, 1914.—T. W. R.)

In order to glean as much knowledge as was within reach, we have endeavoured to obtain as many different samples of radio-active lead as possible, and to determine the atomic weights of the possibly composite element by precisely comparable methods, so as to discover if any

\* From the *Journal of the American Chemical Society*, xxxvi., No. 7.

variation might exist in the chemical equivalents of the different products.

It is a pleasure at the outset to express our deep gratitude to many workers in radio-activity who have furnished us with material. Without this general co-operation, it would not have been possible for us to accomplish anything in so short a time, and we cannot express too highly our appreciation.

In brief, the method of analysis was essentially similar to that used so successfully by Baxter and Wilson in their work upon the atomic weight of ordinary lead (*Proc. Am. Acad.*, 1907, xliii., 363). The chloride was in each case prepared in a state of great purity by recrystallisation in quartz and platinum vessels, after extensive preliminary treatment to eliminate foreign substances. This chloride was carefully dried in a desiccator, and heated to fusion in a stream of hydrochloric acid gas and nitrogen, in the quartz tube of the well-known bottling apparatus which has served in so many similar cases (Richards, "The Faraday Lecture of 1911," *Journ. Chem. Soc.*, 1911, xcix., 1203). The lead chloride was then dissolved in much water, and the chlorine precipitated by silver nitrate. Both the weight of silver required and the weight of the precipitate were determined in the usual Harvard fashion.

As a further check upon the work, control analyses, giving the atomic weight of ordinary lead, were carried out in precisely the same way. These yielded essentially the same value as that found by Baxter and Wilson, and more recently by Baxter and Grover, in work as yet unpublished.

The outcome was striking. There can be no question that the radio-active samples contain another element having an atomic weight so much lower than that of ordinary lead as to admit of no explanation through analytical error, and yet so nearly like ordinary lead as not to have been separated from it by any of the rather elaborate processes to which we had subjected the various samples.

All the materials used in the work were purified with the care usually employed in work of this kind. The silver was made by the precipitation of very pure silver nitrate by ammonium formate, and fused upon boats of the purest lime in hydrogen. The hydrochloric acid gas used for fusion and precipitation was obtained by dropping pure sulphuric acid into chemically pure concentrated hydrochloric acid, furnished by a trustworthy firm and known to be very pure. It was carefully dried and freed from spray by many towers of glass pearls, drenched with sulphuric acid. For precipitation this acid was dissolved in pure water in a quartz flask. The water, and also the nitric acid and other substances used in the work, were purified according to the methods usually employed at Harvard for this purpose.

The description of the preparation of the various samples of lead demands further elaboration. For the first sample of common lead, used as control material, a commercially pure specimen of non-radio-active lead acetate was three times recrystallised from acetic acid solution and the chloride was precipitated, after considerable dilution, by pure hydrochloric acid gas. After the chloride had been many times washed and recrystallised from water, its aqueous solution was filtered through a Gooch-Munroe crucible to eliminate threads of filter paper and other solid impurities. The lead chloride was then twice more recrystallised in a platinum dish and dried over potassium hydroxide (Sample A).

A second sample of ordinary lead chloride was prepared from the purest lead nitrate of commerce in a similar manner. This salt was crystallised three times in glass and twice in platinum, and its aqueous solution was precipitated by pure hydrochloric acid gas in a quartz flask. The salt was thoroughly washed with many treatments of wash water, centrifuged, and finally crystallised three times from a solution weakly acidified with hydrogen chloride in a quartz dish (Sample E).

In order to test the efficiency of crystallisation of lead nitrate as a means of freeing this salt from bismuth (the

impurity most to be feared in our radio-active material), a sample of this salt was mixed with about one-tenth of its weight of bismuth nitrate. After three recrystallisations only a trace of bismuth remained in the crystals, and the fourth removed all that trace which could be detected by qualitative means. There is no doubt, also, that crystallisation of the chloride likewise is a very efficient means of purifying lead.

Our first sample of radio-active lead was very kindly furnished by Dr. Fajans; indeed, his generous initiative in this way made it possible for us to begin. It was from Colorado carnotite and came to us as chloride, containing doubtless traces of iron, bismuth, and other substances. It was, in the first place, recrystallised eight times from the aqueous solution, but even after this treatment was not absolutely white in colour, containing still a trace of iron. Three more crystallisations from hydrochloric acid solution yielded a product of pure whiteness, but because of the slow elimination of the impurities, this sample, G, could hardly be considered as a final product; therefore all the remainder of the material was dissolved in a great volume of water, acidified with nitric acid, and saturated with hydrogen sulphide. The carefully washed sulphide was dissolved in nitric acid, and the nitrate was thrice crystallised (once in platinum) from acid solution. That part of the sulphide oxidised to sulphate was dissolved in ammonium acetate and again precipitated by sulphuretted hydrogen, this process being repeated until practically all of the sulphide had been converted into nitrate. The purified and recrystallised nitrate was precipitated as chloride by purified hydrochloric acid gas as before, and the product was recrystallised twice from dilute hydrochloric acid and once from pure water in a quartz dish (Sample D).

A second source of radio-active lead was very kindly provided by Sir William Ramsay, consisting of residues from pitchblende mined in Cornwall. The brown-grey powder contained ferrous carbonate and many other substances besides lead. This latter element we separated in the first place by the solution of the material in nitric acid, and precipitation with pure sulphuric acid (free from lead), with the addition of alcohol. The sulphate was washed by decantation until practically free from iron, and was dissolved in ammonium acetate and tartaric acid. That portion of the original residue which refused to dissolve in nitric acid was also treated with ammonium acetate to dissolve any lead which might remain as sulphate. This again was precipitated as sulphide. As before, the sulphide was converted into the nitrate, and this salt was treated exactly as in the case of Sample D. The resulting product was designated Sample F, and similar material, prepared later from the same substance with somewhat greater care, was designated as Sample G.

A sample of radio-active lead from Ceylonese thorianite, furnished through the great kindness of Prof. Boltwood, had already undergone considerable purification. From 25 kg. of the thorianite (which contained about three times as much thorium as uranium), 1100 grms. of lead nitrate had been prepared in a state of considerable purity, and 100 grms. of this precious material were placed at our disposal. In its preparation the thorianite had been dissolved in concentrated nitric acid, and the neutralised solution had been precipitated, when moderately dilute, with hydrogen sulphide. The sulphide, after filtration, was then dissolved in hydrochloric acid with the addition of potassium chlorate, and the lead chloride twice recrystallised, converted into nitrate, twice more recrystallised, and came to us at this state. We crystallised it four times more in a quartz dish, and finally converted it into the chloride, which was twice recrystallised from acid solution and once from pure water.

A somewhat similar sample, also from Ceylon, came to us through the kindness of Mr. Miner, Chief Chemist of the Welsbach Light Co., of Gloucester City, N.J., U.S.A. The source was a kilogram of thorianite. This, after solution in dilute nitric acid (the solid residue being separated),

was precipitated with oxalic acid to eliminate the thorium, and the filtrate, made alkaline with ammonia, was precipitated with hydrogen sulphide. But much of the lead had gone into the oxalate precipitate, so that Mr. Miner very kindly recovered this also for us, treating the precipitate with sodium hydroxide and extracting with hot water. From this lye, hydrogen sulphide precipitated a mixture of sulphides which contained much more lead. These two samples of sulphides we now united, dissolved in nitric acid, and crystallised four times as nitrate. The product was converted in the usual manner into the chloride and designated Sample M. A further product made from lead oxidised to sulphate by the action of nitric acid, gave another sample, N.

When the work was well advanced, a new sample of Bohemian uranium-lead was prepared especially for us through the kindness of Dr. Fajans in the following way:—"Das geröstete Erz wurde mit einem Gemenge von  $H_2SO_4$  und  $HNO_3$  (zur Oxydation der vorhandenen Sulfide) behandelt, und dadurch das Uran in Lösung gebracht. Der Rückstand enthielt das Blei als Sulfat, und wurde ihm durch Behandlung mit Aetznatron entzogen, durch Ansäuern wieder ausgefällt, und mittelst Soda in Karbonat verwandelt. Dieses war dann in  $HNO_3$  aufgelöst und das Nitrat kristallisiert worden. Das Präparat wurde unter Anschluss der Möglichkeit einer Verunreinigung durch Blei anderer Provenienz gewonnen." This nitrate (which contained lead oxide and traces of iron) was purified in two different ways. One part was precipitated like Sample F twice as sulphide. This was converted into the nitrate, and was three times re-crystallised in quartz, being finally turned into the chloride as usual (Sample I). Another part was re-crystallised only three times as nitrate, then turned into chloride, and again re-crystallised (Sample K), but according to the results of the analyses it appeared to be as pure as the most carefully treated product. From the lead sulphate which appeared during the solution of the sulphide (Sample I), yet another fraction, L, was made.

Perhaps the most valuable of all our samples (because it came from very pure ore) was a small amount of 3.8 grms. of lead chloride very kindly given us by Prof. Boltwood and Dr. Ellen Gleditsch, of Christiania, Norway, now collaborating with Prof. Boltwood. This product came from the analysis of 120 grms. of the purest selected uraninite from North Carolina, U.S.A. The material was practically of pure radio-active origin, no other lead except that from uraninite itself being included. The sulphides, which had been precipitated from an acid solution of the mineral, were dissolved in nitric acid and the lead separated as chloride. This was crystallised three times from hydrochloric acid solution, and, finally, once more from aqueous solution in a quartz dish, and was designated Sample O.

Another sample, P, was prepared from the filtrates of all the analyses of Sample D. Silver (in addition to other slightly electro-positive elements, if present) was removed by slow fractional electrolysis. The residual electrolyte was repeatedly recrystallised as chloride. It will be noticed that the atomic weight was essentially unchanged.

One of the samples provided by Dr. Fajans came originally from Prof. Giesel, and the other had been prepared with a subsidy from the Heidelberger Akademie der Wissenschaften. We wish to express our grateful thanks to these helpers also. A list of the sources of these various samples may facilitate comparison.

#### Sources of Samples of Lead Chloride.

- Sample A.—Commercial lead acetate, Germany.
- Sample B.—Carnotite, Colorado, U.S.A. (impure), (Fajans).
- Sample C.—Carnotite, almost pure.
- Sample D.—Carnotite the most carefully purified.
- Sample E.—Commercial lead nitrate, America.
- Sample F.—Pitchblende, Cornwall, England (Ramsay).
- Sample G.—Pitchblende, the most carefully purified.

Sample H.—Thorianite, Ceylon (Boltwood).

Sample I.—Pitchblende, Joachimsthal, Bohemia, purest (Fajans).

Sample K.—Pitchblende, preliminary product.

Sample L.—Pitchblende, same as I.

Sample M.—Thorianite, Ceylon (Miner).

Sample N.—Thorianite, later fraction.

Sample O.—Uraninite, North Carolina, America (Gleditsch).

Sample P.—Extremely careful purification of Sample D.

Sample R.—Sample O, further purified.

The consistent method according to which all these samples were analysed has already been briefly described, but perhaps a few points concerning the details deserve discussion.

The desiccator-dried lead chloride was always fused in a current of hydrochloric acid gas, as already stated, in order to be sure that the water was expelled as completely as possible. There was reason to expect that lead chloride thus fused should be neither basic nor containing an important amount of dissolved hydrochloric acid. In support of this conclusion we may cite the neutrality of other chlorides thus fused, as determined by the alkalimetric testing of the dissolved material. (See, for example, Richards and Hönigschmid, *Journ. Am. Chem. Soc.*, 1910, xxxiii., 28; *Sitz. b. Akad. Wiss. Wien.*, 1910, cxix.; *CHEMICAL NEWS*, 1911, civ., 182, 190). It is true, of course, that the specific nature of each chloride is different, and reasoning from analogy is not always safe.

After the lead chloride had been cooled within the bottling apparatus in nitrogen, and this gas had been displaced by air, the fused salt in its platinum boat was pushed into a weighing bottle, in which it was weighed with great accuracy. It was then slowly dissolved in a large bulk of warm water (about 40°) contained in a large Erlenmeyer glass-stoppered precipitating flask. We verified the experience of Baxter that no chlorine is lost during this process.

In spite of our precautions, our samples of lead chloride always exhibited on solution in water a small amount (3 or 4 mgrms.) of white precipitate, which was shown by its immediate solution in a trace of acid to be a basic salt. This may have been partly due to alkali dissolved from the glass. The literature concerning lead chloride suggested that it may be somewhat hydrolysed in aqueous solution. (See, for example, Abegg's "Handbuch," 1909, III., and Part, pp. 648–653; also p. 657). If this is the case, and the trace of basic precipitate came from this cause, it would, of course, have no effect whatever on the result, provided that it was dissolved in a drop of nitric acid before adding silver nitrate. On the other hand, if the basic salt had been formed during fusion, its presence would signify a real loss of chlorine, and the resulting atomic weight of lead would be too high. We obtained from ordinary lead essentially the same values as those found by Baxter and Wilson (and later by Baxter and Grover); therefore the error (if it exists) must apply equally to both sets of determinations. Because lack of time prevented our solving the question, we strove only for comparative results; our problem was not so much to find the true atomic weight of lead, but rather merely to find if the atomic weight of radio-active lead is like that of ordinary lead. The suitable correction, if any is needed, can be applied at any time by subtracting a small quantity from each of our values, which were obtained under precisely similar conditions. Prof. Baxter and his students have previously met with this difficulty in the cases of both lead chloride and lead bromide, and they have been for some time engaged in experiments directed towards solving the problem.

One other correction is involved in three of these analyses, Nos. 21, 25, and 28. In these analyses a combustible black residue, chiefly carbon, of appreciable amount, was left upon dissolving the lead chloride, due doubtless to organic matter taken from the filter-paper

during purification. In each case this was very carefully filtered off and weighed on a Neubauer crucible, and the weight subtracted from the original weight of lead chloride. These three corrections were, respectively, 0.83, 0.66, and 0.20 mgrms. None of the other analyses was entirely free from this carbonaceous substance, but the amount was in every other case less than the least of those just mentioned, and was neglected. Its presence would tend to increase very slightly the observed atomic weight determined from the ratio of lead chloride to silver, but would have no appreciable effect on that referred to silver chloride.

The lead chloride which has been thus weighed and dissolved was precipitated by a weighed amount of silver in the usual way. No unusual precautions were necessary, except that we found that when the solutions were concentrated, lead chloride is more easily occluded by the silver chloride than many other salts (this confirms the experience of Baxter). Working, however, with solutions so dilute that only 1 gm. of lead chloride was contained in 500 cc. of the solution, we were but little troubled from this source. According to Franke the salt must be about 80 per cent dissociated at this dilution (see Abegg's "Handbook," *loc. cit.*). The precipitate after several days comes to a definite and consistent end point, unchanged by further standing. In order to establish the end point with greater exactness, the solubility of the silver chloride was reduced by cooling the solution almost to 0° before removing the samples to be tested. As usual, silver was added to the very nearly precipitated mixture until 25 cc. portions of the supernatant liquid showed, in the nephelometer, the same cloudiness with excess of added chloride in one test-tube as with excess of added silver in the other. The amount of silver exactly equivalent to the chlorine having thus been found, an excess of dissolved silver was added in order to precipitate the dissolved silver chloride, and the whole was filtered with the usual precautions on a carefully weighed Gooch-Munroe crucible with a mat of platinum sponge. The precipitate was dried to constant weight at about 180 deg., and then transferred to a porcelain crucible and fused, in order to dislodge the small remaining trace of water.

In the first place, a number of preliminary analyses were made in order to acquire experience in the method. Of course some of them failed for one reason or another, but they yielded important consequences nevertheless. They showed that the method in our hands yielded with common lead essentially the same results as those obtained by Baxter and Wilson—our values averaging about 207.15 for the atomic weight of lead when it did not contain radio-active material. They showed, moreover, that Colorado carnotite contained lead (Samples C, D) having an atomic weight not far from 206.6 by the same method, and that the lead extracted from English pitchblende (Sample F) had an atomic weight of about 206.9. The preliminary analyses of the radio-active material need not be recounted in detail, because the chloride was not thoroughly purified, and the analytical procedure was not wholly without fault. The analyses of common lead may be briefly recounted.

In four closely agreeing analyses, 16.2966 grms. of fused lead chloride, after complete solution, required 12.6458 grms. of silver for complete precipitation. Thus 100 parts of silver are equivalent to 128.87 parts of lead chloride, and if the atomic weight of silver is taken as 107.88, lead becomes 207.14. Again, in two closely agreeing analyses, 8.17662 grms. of fused lead chloride yielded after due correction 8.4293 grms. of silver chloride. Hence, 100 parts of silver chloride correspond to 97.002 parts of lead chloride, and on the same basis as before lead becomes 207.16. The mean between these two results, 207.15, may be taken as the experimental value for the atomic weight of ordinary lead as observed under these conditions. This result is about halfway between that found by Baxter and Wilson, and that more recently found by Baxter and Grover, but not yet published. Therefore the results indicate that the method had been mastered, and that it

had been giving sufficiently satisfactory results throughout. The agreement of our results by the two methods shows that no important amount of impurity was occluded by the precipitated silver chloride, in agreement with Baxter's outcome.

Most of the analyses thus summarised were made before the radio-active lead was attacked. In the last one, made at the very end of the work, 5.0089 grms. of lead chloride, were fused and dissolved as usual, but before precipitation an amount of the nitrate of radium D (kindly sent by Dr. Fajana) was added, sufficient to make the radio-activity of the mixture correspond approximately to that of Sample D. This was in order to discover whether or not the presence of radio-activity produces serious effect upon precipitation. As the atomic weight calculated from this last result (207.14) was exactly like the average, it is evident that the analytical process is not affected by the mere presence of radio-activity.

Let us now turn to the final results for material obtained from radio-active sources. The work was done with great care, and because of the experience gained in the preliminary trials, the results were more satisfactorily concordant. All the figures concerning these final series are given in the table below, no experiment having been omitted except a single analysis of Sample O, which was made before it was fully purified, and was therefore rejected. Table III. contains the weight of silver needed for each specimen of lead chloride; and Table IV. the weight of silver chloride obtained. The last two columns of each table record the ratios of the substances concerned and the atomic weights of lead computed in the usual fashion from these ratios, assuming the atomic weights of silver and chlorine to be 107.88 and 35.453 respectively.

TABLE III.—Final Results.

Series I.—2Ag : PbCl <sub>2</sub>					
No. of anal.	Sample	Ag.	Corrected weight of fused PbCl <sub>2</sub> in vacuum.	Corrected weight equivalent Ag in vacuum.	Ratio, PbCl <sub>2</sub> : Ag, Atomic weight
16.	D	X	3.87082	3.00984	1.28606 206.56
18.	D	X	5.57331	4.33300	1.28625 206.50
26.	P	Z	5.49412	4.27157	1.28621 206.59
Sum			14.93825	11.61441	Av. 1.28618 206.59
17.	H	X	3.88228	3.01600	1.28723 206.81
19.	H	Y	4.05550	3.15051	1.28722 206.81
20.	H	X, Y	4.05168	3.14788	1.28712 206.79
Sum			11.98946	9.31449	Av. 1.28719 206.81
24.	M	Y	2.80814	2.18162	1.28718 206.81
21.	I	X	3.95052	3.07209	1.28594 206.54
22.	K	X, Y	2.95726	2.29951	1.28604 206.56
Sum			6.90778	5.37156	Av. 1.28598 206.55
23.	G	Y	4.05702	3.15153	1.28732 206.84
29.	R	Z	2.01795	1.56952	1.28563 206.47

Thus the final analyses yielded results essentially like the preliminary ones. The situation will become clearer if the results are all collected and averaged in a summarised table (V.) giving the values of the atomic weight corresponding to each kind of lead.

The result is amazing. Evidently then the chemical equivalents of these different specimens are markedly different from one another. Because the method of analysis was the same in each case, one cannot help thinking that there is a real variation in the chemical equivalents of these samples of lead. Either a large amount of some element having a chemical equivalent nearly as great as lead, or a small amount of an element having a low chemical equivalent must be present, mixed with the substance which we



ordinarily call lead. The fact that all the analyses were carried out by the same method, and that each sample gives consistent results, seems to exclude the effect of analytical error. The nature of this admixture it would be perhaps premature to decide. Clearly it has reactions very much like those of lead, if not exactly identical; for the various processes to which our material was subjected would have eliminated any element widely different. Moreover, the fact that protracted purification had no effect on the atomic weight of any one sample is evidence in the same direction.

TABLE IV.—Final Results.

Series 2.— $\text{PbCl}_2 : 2\text{AgCl}$ .

No. of Anal.	From Series No. 1.	Sample PbCl <sub>2</sub>	Corrected weight of fused PbCl <sub>2</sub> in vacuum.	Corrected weight of fused AgCl in vacuum.	Ratio, PbCl <sub>2</sub> : AgCl.	Weight Ag = 107.53.
40.	16	D	3.87082	3.99879	0.96799	206.59
42.	18	D	5.57331	5.75707	0.96808	206.61
50.	26	P	5.49412	5.67573	0.96800	206.58
m 14.93825 15.43159 Av. 0.96803 206.59						
41.	17	H	3.88228	4.00703	0.96886	206.84
43.	20	H	4.05168	4.18265	0.96870	206.78
Sum 7.93778 8.18968 Av. 0.96877 206.81						
46.	24	M	2.80812	2.89816	0.96894	206.85
45.	22	K	2.95726	3.05475	0.96809	206.61
47.	23	G	4.05702	4.18670	0.96903	206.88
51.	29	R	2.01795	2.08663	0.96767	206.32

TABLE V.—Final Values found for Atomic Weight of Lead from Different Sources.

Lead from North Carolina uraninite (Sample R) ..	206.40
Lead from Joachimthal pitchblende (Sample I, K) ..	206.57
Lead from Colorado carnotite (Samples D and P) ..	206.59
Lead from Ceylonese thorianite (Samples H, M) ..	206.82
Lead from English pitchblende (Sample G) ..	206.86
Common lead .. .. .	207.15

A word should be said concerning the determination of the radio-activity of these various samples, which is an important item in the consideration. The determination was made by means of a quantitative gold-leaf electroscope of the usual type—a square brass box with mica windows, containing a gold-leaf suspended from a flat rod passing through amber. The box was grounded and the electroscope was charged by means of rubbed sealing wax. The material to be investigated was placed on a wooden slide beneath the instrument. The  $\beta$ -rays (which alone were studied) were measured, being allowed to come into the box through a screen of thin tinfoil and aluminium foil. In the first place the time taken for the gold-leaf to fall between two definite points in the micrometer eyepiece of the observing telescope was noticed when no radio-active substance was present; then the times for the various portions were studied under precisely like conditions and compared with the same weight of uranium trioxide. From these times of fall the rates were easily computed, and on subtracting from the rates with radio-active substances, the rate when nothing was present, the comparative values for the various substances were obtained. Immediately after purification, of course, the specimens were practically non-radio-active, because during crystallisation radium E, which is the chief source of the  $\beta$ -rays, goes into the mother liquor. As is shown by the figures for our Sample D at the top of Table VI., the radio-activity of freshly prepared crystals steadily increased in the usual curve until the maximum was attained in about thirty days. Radium E is then in equilibrium with radium D. The table gives, in its lower part, a comparison of the radio-activity of the different samples. It

will be seen that Sample D was the most radio-active, Sample O next, and Samples F and G the least. An old sample of uranium trioxide is included to give an idea of the magnitude of the effect.

TABLE VI.

Sample of PbCl <sub>2</sub> , 1.5 g.	Time in days	Time in seconds elapsed of fall of gold-leaf crystal with pre-irradiation.	Rate of fall per minute.	Natural fall of leaf per minute.	Corrected rate of fall with preparation.
D .. .. .	0.2	472	0.127	0.043	0.084
D .. .. .	1.2	203	0.296	0.035	0.261
D .. .. .	2.0	144	0.417	0.035	0.378
D .. .. .	4.1	91	0.659	0.036	0.623
D .. .. .	5.2	78	0.769	0.041	0.728
D .. .. .	6.1	71	0.845	0.042	0.803
D .. .. .	7.0	69	0.870	0.043	0.827
D .. .. .	8.9	64	0.942	0.037	0.905
D .. .. .	12.1	56	1.072	0.039	1.033
D .. .. .	14.3	53	1.133	0.043	1.090
D .. .. .	16.3	49	1.220	0.039	1.188
D .. .. .	18.0	49	1.220	0.039	1.188
D .. .. .	27.0	43	1.396	0.046	1.350
D .. .. .	40.0	43	1.396	0.045	1.351
R(x) .. .. .	>200	47	1.278	0.031	1.247
1.27 g.					
D .. .. .	59.0	53.0	1.132	0.045	1.087
F .. .. .	40	265.0	0.226	0.045	0.181
G .. .. .	24	270.0	0.222	0.045	0.177
H .. .. .	35	204.0	0.294	0.045	0.249
I .. .. .	?	182.5?	0.329?	0.045	0.284?
M .. .. .	29	257.5	0.234	0.045	0.189
O .. .. .	20 ±	85.0	0.707	0.045	0.662
UO <sub>3</sub> standard >	1000	628.0	0.095	0.045	0.050

(x) This sample was taken from the impure original lead chloride from carnotite, as we had received it. The slightly lower value is probably due to another size of crystals and the non-radio-active impurities.

Although in general the samples of lead having greater radio-activity show less atomic weight, the decrease in the atomic weight is not exactly proportional to the radio-activity. For example, preparation O (the same material as preparation R) is distinctly less radio-active than Sample D, although the atomic weight exhibited by O is decidedly more divergent from the usual value than that exhibited by D. The rates of fall for 1.27 g. of O and D, both twenty days old, were respectively 0.66 and 0.99, whereas the deficiencies in the atomic weights of these samples were respectively 0.75 and 0.56. The irregularity suggests the presence of more than two variables. More data are clearly necessary for a definite conclusion. The attempt to explain the relationship will therefore be deferred.

The spectroscopic examination of one of these samples (Sample D) was conducted with the generous help of Professor Baxter in his admirable Fery quartz spectrograph. Very well-defined photographs of the ultra-violet portion of the spectrum of our Sample D (after it had been recovered from an analysis, and therefore contained a trace of silver) were taken on a film, side by side with similar photographs of Baxter's purest lead. The parallelism of the two, both as regards the number of lines and the intensity of the lines was complete throughout the whole field, from wave-length  $0.4\mu$  to the extreme ultra-violet visible in this instrument (about  $0.200\mu$ ) except that the characteristic silver lines  $0.3281\mu$  and  $0.3383\mu$  were clearly depicted and the prominent copper lines  $0.3248\mu$  and  $0.3274\mu$  were faintly visible. The latter had an intensity corresponding, on a very conservative estimate, to 1 part of copper in 100,100 parts of lead, determined by comparison with the spectrum of lead containing known traces of copper—an amount far too minute to have any effect on the atomic weight. The silver doubtless came from the analytical operations, as already said; and its



manifest appearance is good evidence of the great sensitiveness of the spectrometer. No shifting or obvious broadening of any of the lines was observed, but it would not have been possible to see a very slight effect of this kind.

Thus it appears that the lead from radio-active sources, having an atomic weight of 206.6, gives essentially the same ultra-violet spectrum as ordinary lead, having an atomic weight (determined by the same method in parallel analyses) of 207.15.

The obvious inference to be drawn from this amazing result is that one of four alternatives must hold true. Either the unknown substance, which is mixed with ordinary lead and produces the lower atomic weight, has the same spectrum as lead itself; or else it gives no lines whatever in the ultra-violet range of this photograph; or else the presence of a large bulk of lead hides or aborts the spectrum of the foreign admixture; or else ordinary lead is a similar medley in somewhat different proportions. It is perhaps premature to decide between these alternatives, but all are of interest, the first and last of course being the most revolutionary.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ALCHEMICAL SOCIETY.

Ordinary Meeting, January 8, 1915.

Mr. H. STANLEY REDGROVE, B.Sc., F.C.S., Acting President, in the Chair.

A HIGHLY interesting paper on "*The Philosophical Channels of Alchemical Tradition*" was read by Mr. GASTON DE MENGEL.

Mr. De Mengel opened his paper with a description of what he termed the "white" and the "black" traditions, their interaction and commingling. Alchemy, he observed, early came under a ban, owing to its alliance with magic—product of the "black" tradition—from which, however, it soon freed itself. He mentioned various philosophical soils in which the tree of alchemy had grown, and dealt particularly with Greek philosophy as it flourished in Alexandria in the third century A.D. Alchemy, he considered, owed much to Platonism and Neo-platonism—Plato, through Pythagorism, serving to link Greek free-thought to the ancient Orphic mysteries and authoritative religion. Its mind, he said, was essentially intuitive; the alchemists were weak in their dialectic, and their experiments—or rather their descriptions of them—are not to be relied on. The value of alchemy lay rather in what revelation it might yield us of the esoteric doctrines, imbued with all the fervour of mysticism, and for which it ultimately came to serve as one of the repositories.

The full text of the lecture and a *résumé* of the discussion which followed will appear in the January number of the Society's Journal.

## NOTICES OF BOOKS.

*Elementary Practical Chemistry.* By J. E. MYERS, M.Sc. (Vict.) and J. B. FIRTH, M.Sc. (Vict.). London: Charles Griffin and Co., Ltd. 1914.

THE material in this book has been carefully selected to suit the requirements of students of medicine and pharmacy. General methods of preparation are first described, so as to give practice in easy manipulation such as precipitation, filtration, &c. Qualitative analysis, including the detection of the constituents in simple mixtures, is then treated, and elementary gravimetric and volumetric work follow, together with a little gas analysis. The chemical reactions of some organic compounds are

described, and a scheme is given for the identification of the commoner organic compounds. The book contains no superfluous matter whatever, and the directions are always clear and concise; it will undoubtedly be found useful as an introductory practical book by students other than those for whom it is specially intended.

*The Elements of Physical Chemistry.* By J. LIVINGSTON R. MORGAN, Ph.D. Fifth Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

THIS is a useful general review of physical chemistry, which without going very deeply into any particular branch gives a very clear summary of the whole subject, and prepares the student for the use of more detailed and exhaustive treatises. The treatment is as non-mathematical as possible, and the needs of the student who is working without a teacher are specially considered. The fifth edition has on the whole been very much enlarged, although certain parts have been curtailed. Thus, the discussions of the phase rule and of colloidal solutions have been restricted, the reader being referred to special works on the subjects for fuller details. The system of notation has been changed throughout, in order that it may agree with that recently adopted by the International Commission for the Unification of Physico-Chemical Symbols.

*The Manufacture of Organic Dyestuffs.* Authorised Translation from the French of ANDRÉ WAHL, D. ès Sc., by F. W. ATACK, M.Sc. Tech. (Mane.), B.Sc. (Lond.), A.I.C. London: G. Bell and Sons, Ltd. 1914.

THE appearance of a book upon the manufacture of aniline dyes is most opportune at the present moment, and it should be assured of a cordial reception, especially as it is in every way well planned and thoroughly practical. It will be found excellent for technical students, for whom it is specially written, and also for practical men, provided that they have a good general knowledge of organic chemistry. The raw materials of the dyestuffs and the treatment to which they are subjected are first discussed, and the general principles of the reactions by which they are converted into the intermediate products are outlined. Then the dyestuffs classified according to the chromophore present are described in full. The application of them is treated only very shortly, but all the details of manufacture, quantities, costs, &c., are taken from actual practice.

*The Effect of the War on Commercial Engagements.* By F. GORE-BROWNE, M.A., K.C. London: Jordan and Sons, Ltd. 1914.

GREAT Britain has been so long at peace with all the Great Powers of the World that there is considerable ignorance in all circles concerning the laws regarding the relations and contracts of British subjects with alien enemies. This general discussion of the effects of the war upon commercial engagements will be very helpful to the public; it outlines in clear, and as far as possible non-technical language, the exact state of affairs relating to the position of aliens and the validity of contracts made with them, and a summary is also given of the emergency legislation and of the proclamations and statutory rules and orders which were issued.

*The Examination of Lubricating Oils.* By THOS. B. STILLMAN, M.Sc., Ph.D. Easton, Pa.: The Chemical Publishing Co. 1914.

THIS book gives a systematic and concise account of methods of testing lubricants of all kinds. Clear directions are given for the performance of the most rapid and simple tests, and different kinds of apparatus are illustrated and their use fully described. The book will probably be found most useful by American chemists, for American

methods are chiefly described; for instance, Redwood's viscometer is only briefly alluded to, although a diagram of it is given. An article by P. H. Conradson on Apparatus for the Examination and Study of the Behaviour of Valve and Cylinder Oils and other Petroleum and Lubricating Oils in Saturated and Superheated Steam, Carbon Dioxide, and other Gases, is included.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Bulletin de la Société Chimique de France.*  
Vol. xv-xvi., No. 15, 1914.

**Fluorine in Mineral Waters.**—Armand Gautier and P. Clausmann.—Fluorine exists in all mineral waters, those of eruptive origin being richest in it. Thermal sodium bicarbonate waters contain the most fluorine per litre. Cold calcium sulphate waters, whatever their superficial origin, may contain about 2 mg. of fluorine per litre. In mineral waters of the same kind the proportion of fluorine does not seem to be connected with the temperature, increasing with it, but in waters of the same origin, whether thermal or not, the quantity of fluorine generally increases with the salinity. In sea-water the amount of fluorine varies a little with the station and the depth; it oscillates about 0.3 mg. per litre.

**Anhydrous Protosulphides of Alkaline Metals.**—E. Rosta and N. Costeau.—The authors thought that they would get good results in preparing the protosulphides of alkaline metals by the direct combination of sulphur with a large excess of the metal, which could subsequently be removed by distillation *in vacuo*. If the sulphides, like the oxides, were soluble in the corresponding metals they would be deposited during the evaporation. The experiment is, however, much less easy to perform with the sulphides than the oxides. Solid sulphur does not appear to react on fused potassium, and hence it is necessary to heat the two substances to 200°–300° in a sealed vacuum tube. The protosulphides are white or slightly yellow at the ordinary temperature. When heated to about 300° they become more yellow. They are much less soluble in the corresponding metals than the oxides, and they crystallise with more difficulty. They are more stable than the protoxides and are not affected by light nor decomposed by anhydrous ammonia in the cold. They are very readily oxidised. In the cold sodium protosulphide is only slowly attacked by damp air, while the others rapidly deliquesce; when thrown into water they dissolve, with evolution of heat.

**Basic Sulphates of Copper.**—MM. Fonze-Diacon.—When a solution of sodium carbonate is poured gently into a constantly stirred solution of copper sulphate, when the solution is rich in the latter a tetrahydrated tetracupric sulphide is formed. As the concentration diminishes a pentacupric sulphate is obtained. Finally, when the sodium carbonate is present in excess it decomposes the basic sulphates, giving the hydrocarbonate of copper. When the supernatant liquid is left exposed to the air carbon dioxide is disengaged and blue tetracupric sulphate containing five molecules of water, or green tetracupric sulphate containing four molecules of water, is deposited according to circumstances.

**Preparation of Anhydrous Nickel Bromide and one of its Compounds with Ethyl Oxide.**—F. Ducelliez and A. Raynaud.—Anhydrous nickel bromide is easily prepared by the action of an ethereal solution of bromine upon the powdered metal. The action begins at the ordinary temperature, and the metal is rapidly transformed into a brown powder which when heated to 150° furnishes light yellow anhydrous  $\text{NiBr}_2$ , readily soluble in water. As in the case of manganese a compound with ether is formed, which facilitates the union of bromine with these

metals. It is a light brown compound of formula  $\text{NiBr}_2 \cdot \text{C}_4\text{H}_{10}\text{O}$ .

**Bromination of Benzene, Toluene, and Xylene.**—F. Ducelliez, L. Gay, and A. Raynaud.—Manganese is a very good catalyst for bromination, and can advantageously be used to replace already known catalysts. It furnishes an interesting example of catalytic action, on the part of an uncombined metal. Its action does not appear to be attributable to any traces of aluminium it may contain. The homologues of benzene very readily give derivatives containing bromine substituted in the nucleus without the intervention of a catalyst.

**Decomposition of Aspyrin by Water.**—W. E. Tsakalotos and S. Horsch.—The decomposition of aspyrin by water at the ordinary temperature is very slow; it is complete after about 100 days. Acids ( $\text{H}^+$  ions) exercise a catalytic influence on this decomposition. It is accelerated by hydrochloric and sulphuric acids, and the acceleration is greater with the stronger acid, hydrochloric acid. Acetic acid accelerates the action up to about the eighth day and then retards it. Citric acid acts in the same way.

**Cis-Caronic Acid and its Derivatives.**—R. Locquin.—Cis-caronic acid melts at about 174°, when its melting-point is determined by using a capillary tube heated in a bath of sulphuric acid, but its instantaneous melting point, taken over mercury, is 186°. Terebic acid, with which it might be confused, always melts at 174°, whether it melts slowly or quickly. The two acids can also be distinguished by the different melting-points of corresponding ethers. The best way to prepare caronic anhydride is to boil cis-caronic acid with excess of acetyl chloride, acetic anhydride, or thionyl chloride. When the mass is distilled the pure anhydride, boiling exactly at 135–137° under 14 mm., is obtained. When a benzene solution of this anhydride is mixed in equimolecular proportions with a benzene solution of aniline the corresponding phenylamide acid is obtained.

## MISCELLANEOUS.

**Messrs. Read, Holliday, and Sons, Ltd.**—In a booklet recently issued by this firm an interesting account is given of the foundation and early history of the firm, and their works are shortly described. The firm is one of the most important manufacturers of coal-tar colours and synthetic dyes in Great Britain, and has recently established a department for preparing drugs and fine chemicals, a branch of manufacturing chemistry which has hitherto been much neglected in England.

## MEETINGS FOR THE WEEK.

- MONDAY, 25th.**—Royal Society of Arts, 8. (Cantor Lecture). "Oils, their Production and Manufacture," by Dr. F. Mollwo Perkin.
- TUESDAY, 26th.**—Royal Institution, 3. "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S.  
— Royal Society of Arts, 4.30. "The Economic Development of British East Africa and Uganda," by Major E. H. M. Leggett, R.E., D.S.O.
- WEDNESDAY, 27th.**—Royal Society of Arts, 8. "Portrait Painting," by Hon. John Collier.
- THURSDAY, 28th.**—Royal Institution, 3. "Modern Theories and Methods in Medicine," by H. G. Plimmer, F.R.S.  
— Royal Society. "Influence of Salt Concentration on Hemolysis," by W. W. C. Topley. "The Life-cycle of Cladocera, with Remarks on the Physiology of Growth and Reproduction in Crustacea," by G. Smith. "Investigations on Protozoa in relation to the Factor Limiting Bacterial Activity in Soil," by T. Goodey. "The Mesodermic Origin and the Fate of the so-called Mesoderm in Petromyzon," by S. Hata. "Influence of Direction of Homodromous and Heterodromous Electric Currents on Transmission of Excitation in Plant and Animal," by J. C. Boss.
- FRIDAY, 29th.**—Royal Institution, 9. "Gaseous Explosions," by Dr. Dugald Clerk, F.R.S.
- SATURDAY, 30th.**—Royal Institution, 3. "Aerial Navigation—Scientific Principles," by R. T. Glazebrook, C.B., F.R.S., &c.

# THE CHEMICAL NEWS.

Vol. CXL, No. 2879.

## THE SANDY SOIL OF SYLVAN BEACH, NEW YORK.

By NICHOLAS KNIGHT, Cornell College.

THE locality is the eastern shore of Oneida Lake in Central New York. The entire territory was formerly the lake bottom, at the time when the water was discharged into the Mohawk River. An elevation of the land seems slowly to have taken place, the lake was projected farther north and the water now reaches Lake Ontario through the Oneida and the Oswego Rivers. The soil of the territory for 25 or 30 square miles is almost a pure sand, and is unadapted to agricultural purposes. There are numerous forest trees, including pine, oak, hemlock, and maple upon the sand, that attain a slow growth, and there is dense shrubbery and undergrowth. It seems lacking in fertility, and it does not add materially to the wealth of its owners.

Sylvan Beach has become a popular summer resort, and its population during the season reaches about 5000. There is no system of sewage disposal at the resort, but it was long ago observed that all forms of organic matter in the sand very quickly decomposes. It is not necessary to remove the sewage from the cesspools, but in some way it is taken care of in the sand. Refuse from the kitchen, including corn-husks and cobs, banana and orange peels, apple and potato parings, quickly disappear, and in the course of a few weeks a black substance is found in their place. The leaves of the trees when buried in the soil soon are transformed into a black vegetable mould.

It occurred to us, as for a number of years we had observed these rapid changes in the organic refuse buried in the soil, that possibly there is a considerable quantity of iron in the sand which oxidises the refuse material and serves as a carrier of oxygen.

Accordingly we made an analysis of two different portions of the soil.

	Per cent.
(1). SiO <sub>2</sub> .. .. .	91.83
Al <sub>2</sub> O <sub>3</sub> .. .. .	6.28
Fe <sub>2</sub> O <sub>3</sub> .. .. .	1.71
CaO .. .. .	0.65
MgO .. .. .	0.39
K <sub>2</sub> O .. .. .	0.04
Na <sub>2</sub> O .. .. .	0.03
Nitrogen .. .. .	—
Phosphate .. .. .	—
CO <sub>2</sub> .. .. .	—
Total .. .. .	100.98

(2). SiO <sub>2</sub> .. .. .	94.48
Al <sub>2</sub> O <sub>3</sub> .. .. .	2.17
Fe <sub>2</sub> O <sub>3</sub> .. .. .	1.76
CaO .. .. .	1.17
MgO .. .. .	0.47
K <sub>2</sub> O .. .. .	0.04
Na <sub>2</sub> O .. .. .	0.07
Nitrogen .. .. .	—
Phosphate .. .. .	—
CO <sub>2</sub> .. .. .	—
Total .. .. .	100.16

No. 1 was taken from a depth of 18 inches, about 50 rods from the lake, while No. 2 was close by the shore. No. 1 presumably arose from the lake centuries before

No. 2, and so the elements have had a longer time to work it up into a soil. It is finer grained than No. 2, yet the analysis does not reveal the difference we expected. The elements of soil fertility, phosphorus, nitrogen, and potash are sadly lacking in both specimens. The analysis scarcely discloses why organic matter so quickly decays in the soil. We expected to find a much higher percentage of iron in both samples by which to explain the rapid disappearance. Doubtless the iron present is an important factor in the changes, but it does not explain all. The bacteria content must also be small, because there is little, if any, nitrogen present. Possibly the greatest reason for the change is the free access of air. The sand does not form a hard crust on top in any kind of weather, and the atmosphere is always accessible. Cameron says ("The Soil Solution," p. 53):—"The atmosphere within the soil contains normally a smaller proportion of oxygen than does the air above the soil. Rain, in falling through the air, absorbs or dissolves relatively more oxygen than nitrogen. Therefore when the rain-water has penetrated the soil to any considerable depth, there should be, and probably is, a liberation of dissolved oxygen into the atmosphere of the soil interstices."

By the free use of leaves, barnyard manure, and various forms of organic refuse it seems to us that a fairly rich and productive soil might be formed in this territory. The experiment might prove interesting and profitable. As the population of the country increases and land values multiply, it will be necessary to use all available land and to bring it to the highest degree of cultivation.

There are many agricultural problems in the Empire State awaiting solution. Farm land with good or fairly good buildings is selling for 9 or 10 dols. an acre, and that too within easy distance of some of the largest cities and the best markets on the western hemisphere. The land will respond to proper treatment, and the original fertility will be restored. This is an important work which can be done only by those who make a special study of the subject and acquire a suitable training in the agricultural schools.

We desire to express our thanks to Mr. Euclid Marston for making the analyses described in this paper.

## CÆSIUM ALUM AND ITS PROPERTIES.

By EDWARD HART and HENRY B. HUSELTON.

SINCE the discovery of cæsium by Bunsen in 1860, its compounds have been investigated at various times, but a broad field for research still exists. The alum is one of the many compounds of cæsium that offer an opportunity for original work.

Cæsium alum was studied by Redtenbacher in 1865 (*Y. Prakt. Chem.*, 1865, xciv., 442), by Carl Setterberg (*Ann.*, 1882, ccxi., 100) in 1881, and by Locke (*Am. Chem. Journ.*, 1901, xxvii., 166) in 1901. Setterberg compared the solubility of rubidium and cæsium alums at eight different temperatures. Locke, in his work on an examination of all possible alums, gives the solubility of cæsium alum at four temperatures, and two of these differ from the results obtained by Setterberg. His other values were found at temperatures not given by Setterberg, and therefore must be compared with interpolated figures. They are not the same.

The alum used was prepared from pollucite by treatment with sulphuric and hydrofluoric acids, followed by solution in water and recrystallisation. The pollucite used appeared to contain zirconium. A considerable amount of jelly-like material separated, probably a zirconium compound, which was not further examined. This renders filtration difficult and tedious. The crude alum had a slight yellow colour, due to ferric iron, which was removed by recrystallisation from water containing sulphur dioxide. The crystals finally obtained were examined spectro-

scopically, and found to be free from rubidium and potassium. These crystals were used in the following:—

TABLE I.—Solubility Determinations.

No.	Temp. Grms.	Residue per 100 g. H <sub>2</sub> O. Gms.	No.	Temp.	Residue per 100 g. H <sub>2</sub> O. Gms.
1.	7°	0.255	10.	47°	1.173
2.	19	0.422	11.	49.25	1.387
3.	22	0.426	12.	50	1.417
4.	22.5	0.435	13.	56	1.86
5.	24	0.474	14.	60	2.06
6.	29.5	0.571	15.	66	2.798
4.	31.5	0.607	16.	66	2.85
8.	40	0.865	17.	68	3.13
9.	41	0.879	18.	80	5.78

TABLE II.—The Solubility of Anhydrous Cæsium Alum, AlCs(SO<sub>4</sub>)<sub>2</sub> in water.

Temp.	Grms per 100 g. H <sub>2</sub> O	Temp.	Grms per 100 g. H <sub>2</sub> O.
0°	0.19	51°	1.39
1	0.20	52	1.45
2	0.21	53	1.51
3	0.22	54	1.58
4	0.23	55	1.65
5	0.24	56	1.71
6	0.25	57	1.77
7	0.26	58	1.86
8	0.27	59	1.92
9	0.28	60	2.06
10	0.29 (a)	61	2.14
11	0.30	62	2.25
12	0.31	63	2.37
13	0.32	64	2.50
14	0.34	65	2.65
15	0.35	66	2.78
16	0.36	67	2.96
17	0.38 (a)	68	3.13
18	0.39	69	3.34
19	0.40	70	3.50
20	0.41	71	3.67
21	0.41	72	3.85
22	0.43	73	4.07
23	0.45	74	4.30
24	0.47	75	4.50
25	0.49 (a)	76	4.72
26	0.50	77	4.95
27	0.51	78	5.15
28	0.52	79	5.40
29	0.55	80	5.78
30	0.57	81	6.05
31	0.59	82	6.4
32	0.60	83	6.7
33	0.62	84	7.0
34	0.65	85	7.4
35	0.69 (a)	86	7.7
36	0.72	87	8.0
37	0.75	88	8.3
38	0.77	89	8.6
39	0.80	90	8.8
40	0.85	91	9.0
41	0.87	92	9.2
42	0.91	93	9.5
43	0.96	94	9.9
44	1.01	95	10.1
45	1.06	96	10.4
46	1.10	97	10.8
47	1.17	98	11.1
48	1.21	99	11.5
49	1.27	100	12.0
50	1.30		

(a) Given by Setterberg.

NOTE.—0° to 40°, accurate as given; 40° to 80°, first decimal correct; 80° to 100°, extrapolated, approximately correct.

The first five values of Setterberg coincide almost exactly with ours. Above 10° his values are less. In Table II., the values from 0–7° were obtained by interpolation, using Setterberg's values for 0°. From 80–100° they were calculated by extrapolation, and are only approximately correct.

*Specific Gravity.*—The specific gravity of the hydrated alum was obtained by weighing in 95 per cent ethyl alcohol, in which it is insoluble. Two determinations were made, giving 1.96 and 1.93; average 1.945.

*Melting-point.*—The hydrated crystals in powder were enclosed in the usual capillary tube, which was heated in sulphuric acid. After the alum had melted, a fine capillary was inserted, and the solidifying point determined by drawing on the capillary until it broke. The following determinations show that the alum melts at 117°:—

Beginning	End.	Solid	Average
115°	115°	115°	116.5
116	118	117	117
117	118	116	117

Average .. 117      118      116      117

The melting-point of cæsium alum has been determined as follows:—

Tilden (*Journ. Chem. Soc.*, 1884, xlv., 266 .. 106°)

Erdman (*Arch. Pharm.*, cccxxii., 3) .. 120.5

Locke (*Am. Chem. Journ.*, 1901, xxvi., 183) .. 122°

—*Journal of the American Chemical Society*, xxxvi., No. 10.

## THE ATOMIC WEIGHT OF LEAD OF RADIO-ACTIVE ORIGIN.\*

By THEODORE W. RICHARDS and MAX E. LEMBERT.

(Continued from p. 47).

THAT lead should be composed of a mixture of substances of different origin but similar properties is, after all, possibly not so revolutionary a proposition as might appear at first sight. Rare earths are often very similar in properties, and large amounts of material and very patient fractionation are necessary to separate them. Why should not the same thing be true of several of the commoner elements? The only practical difference besides the presence of radio activity seems to lie in the fact that in the present case the intruders produce no obvious change in the ultra-violet spectrum. But if all lead is a mixture, this might be expected.

At first sight one might be inclined to feel that the irregularity in the quantitative results above described should diminish one's respect for the significance of atomic weights in general, but further thought shows that this is a superficial view. If the results which we have obtained really indicate that several kinds of lead, having the same properties and spectrum, may be mixed together and not separated chemically, it is evident that the atomic weight becomes almost the only criterion, except radio activity, capable of detecting the admixture and tracing the factors to their source. Thus the study of atomic weights is shown to be not less but more significant than it had been before. To emphasise this point we may, perhaps, quote two paragraphs, written seven years ago, long before the theory under discussion had been proposed, and when such ideas were of a rather heretical character:—

"Are the supposed constant magnitudes to be measured in chemistry really variable . . . ? If they are thus variable, is it worth while to expend much labour in determining the values which they happen to possess at any one time under any one set of conditions?"

\* From the *Journal of the American Chemical Society*, xxxvi., No. 7.

"The question as to whether or not the supposed constants of physical chemistry are really not constants, but are variable within small limits, is of profound interest, and of vital importance to the science of chemistry and to natural philosophy in general. If this latter alternative is true, the circumstances accompanying each possible variation must be determined with the utmost precision, in order to detect the ultimate reason for its existence. As Democritus said long ago, 'the word chance is only an expression of human ignorance.' No student of natural science who perceives the dominance of law in the physical universe would be willing to believe that such variations in a fundamental number could be purely accidental. Every variation must have a cause, and that cause must be one of profound effect throughout the physical universe. Thus the idea that the supposed constants may possibly be variable adds to the interest which one may reasonably take in their accurate determination, and enlarges the possible field of investigation instead of contracting it" (Richards, Berlin Inaugural, *Science*, N.S., 1907, xxvi., 562; also *Die Umschau*, 1909, xiii., 542, translated by F. Haber).

This matter has received not only speculative but also experimental treatment at Harvard. For many years the possibility that samples of a given element from different sources might have different atomic weights had been considered and investigated, but never before with a positive outcome. In the first investigation of the atomic weight of copper undertaken by one of us as long ago as 1887 (Richards, *Proc. Am. Acad.*, 1887, xxiii., 179), samples of copper obtained from Germany and from Lake Superior were found to give precisely the same atomic weight for this element. More recently the question was revived, and in 1897 specimens of calcium carbonate were obtained from Vermont, U.S.A., and from Italy, in order to discover whether or not the calcium in these two widely separated localities had the same atomic weight. Not the slightest difference was found between them (Richards, *Four. Am. Chem. Soc.*, 1902, xxiv., 374). Again, in a very elaborate investigation on the atomic weight of sodium (Richards and Wells, *Carnegie Institut. Wash. Pub.* 28, 1905), silver was obtained from several distinct sources and sodium chloride was obtained partly from several different samples of German rock salt, and partly from the salt pumped from the Solvay Process Company's mines at Syracuse, N.Y. These preparations, differing widely in the steps of manufacture and in geographical source, all yielded essentially the same atomic weights within the limit of error of the process. (Even if both specimens of salt came originally from a Silurian ocean, the time and condition of deposition were probably widely different). Yet more recently Baxter and Thorvaldson (*Four. Am. Chem. Soc.*, 1911, xxxiii., 337), with the same possibility in mind, determined the atomic weight of extra-terrestrial iron from the Cumpas meteorite, which gave a result identical with ordinary iron within the limit of error of experimentation. From these researches it would seem probable that even if an unusual eccentricity may be exhibited by lead, most elements do not as a rule differ from any such cause of uncertainty. Baxter and Grover are now engaged in the examination of ordinary lead from different geographical sources. Perhaps this also contains more than one component, as suggested above.

It would perhaps be premature to indulge in further hypothetical reasoning concerning the nature of this extraordinary phenomenon, but the nature of the variation unquestionably points in the direction of the hypothesis of Fajans and of Soddy.

This paper must be looked upon only as a preliminary one. More time, larger amounts of material, and more chemical experimentation are needed in order to be sure that the reactions of the unknown contaminating element and lead are wholly identical. We hope and intend to continue the study and solve the highly interesting questions which it presents.

We are greatly indebted to the Carnegie Institute of Washington for much of the apparatus and material used in this research.

#### Summary.

In this paper a description is given of parallel experiments determining the equivalent weights of various samples of lead chloride obtained from different sources. It was found that all of the radio active specimens possess a lower atomic weight than ordinary lead, as determined under identical conditions, the deficiency in one case amounting to as much as 0.75 of a unit.

No simple linear quantitative relationship between the exact amount of radio-activity and the atomic weight was found. The radio-activity of the various samples was compared by means of the quantitative electroscope.

The ultra-violet spectrum of a typical radio-active sample was compared with that of ordinary lead, with the help of G. P. Baxter, in a quartz spectrograph. No difference was found between the spectra of these specimens, except for a trace of copper too small to affect the result and a negligible trace of silver known to have been present. The inference seems to be that radio-active lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by chemical means. This substance cannot be identified in the ultra-violet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or absorbed by that of lead.

This amazing outcome is contrary to Harvard experience with several other elements, notably copper, silver, iron, sodium, and chlorine, each of which seems to give a constant atomic weight, no matter what the geographical source may have been. No attempt is made here to discuss the theoretical aspects of the facts presented, but attention is called to their qualitative agreement with the hypothesis of Fajans and of Soddy.

### THE FREEZING-POINT OF SOME ABNORMAL MILKS.\*

By J. B. HENDERSON, F.I.C., and L. A. MESTON.

ON May 15, 1914, among several samples of milk submitted for analysis in the Government Chemical Laboratory, Brisbane, by a food inspector, were two, from different sources, which gave on analysis the results shown in Table I.

TABLE I.

	No. 4349. (Six cows).	No. 4353. (Two cows).
Total solids (per cent) .. ..	11.60	11.69
Fat (per cent) .. ..	3.86	3.90
Solids not fat (per cent) .. ..	7.74	7.79
Ash (per cent) .. ..	0.80	0.78
Nitrogen (per cent) .. ..	0.49	0.47
Chlorine in ash (per cent) .. ..	22.6	22.6
Chlorine in ash as NaCl (per cent) .. ..	37.2	37.2
Ratio—Ash : NaCl .. ..	2.68	2.68
Ratio—Ash : Solids not fat .. ..	10.3	10.0
Freezing-point (°C.) .. ..	0.55	0.54
Composition of solids not fat—		
Milk sugar (per cent) .. ..	49.2	51.4
Proteids (per cent) .. ..	40.3	38.4
Ash (per cent) .. ..	10.3	10.0

The fat, solids not fat, and nitrogen are all low, while the ash is just a shade above normal and the proportion of chlorine in the ash much above the normal. The freezing-point is, however, in each case practically normal.

\* Read before the Royal Society of Queensland, November 9, 1914.



TABLE II.—Herd A (Six Cows).

Cows.	1.	2.	3.	4.	5.	6.	Mixed milk.	Normal milk
Yield (quarts)	2	2	1	4	3	3	15	
Total solids (per cent) .. ..	12.9	12.8	9.2	11.9	13.8	12.1	12.4	12.9
Fat (per cent) .. ..	5.0	4.0	2.8	3.7	4.6	3.7	4.0	4.0
Solids not fat (per cent) .. ..	7.9	8.8	6.4	8.2	9.2	8.4	8.4	8.9
Ash (per cent) .. ..	0.88	0.70	0.89	0.69	0.77	0.74	0.76	0.75
Nitrogen (per cent) .. ..	0.62	0.50	0.48	0.47	0.58	0.50	0.52	0.52
Chlorine in ash (per cent) .. ..	22.2	14.4	28.7	19.0	17.2	19.7	19.2	14.0
Chlorine calc. as NaCl (per cent)	36.5	23.7	47.3	31.3	28.3	32.4	31.6	23.0
Ratio—Ash : NaCl .. ..	2.7	4.2	2.1	3.1	3.2	3.0	3.1	4.6
Ratio—Ash × 100 : Solids not fat	11.1	7.9	13.9	8.4	8.3	8.8	9.0	8.3
Freezing-point (°C.) .. ..	-0.545	-0.545	-0.560	-0.552	-0.550	-0.550	-0.550	-0.555
Composition of solids not fat—								
Milk sugar (per cent) .. ..	38.8	55.8	35.2	55.0	51.4	53.2	51.4	52.8
Proteids (per cent) .. ..	50.0	36.2	47.8	36.5	40.2	37.0	39.5	37.8
Ash (per cent) .. ..	11.1	7.9	13.9	8.4	8.3	8.8	9.0	8.3

At first glance the analytical results seem to indicate that each milk is a milk which has been watered, and a little common salt added to lower the freezing-point again to normal. Added water, if calculated on the basis of a normal solids not fat of 8.9 per cent in sample "A" would reach 13 per cent. The excess of salt present in the sample would lower the freezing-point to cover an addition of 12.5 per cent of added water. Similarly, added water in sample "B" if calculated on the 8.9 solids not fat standard would reach 12.5 per cent, while the excess of salt present would lower the freezing-point to cover 12 per cent of added water. In each case there is a remarkable agreement between the deduction made from the solids not fat standard and that from the excess of salt.

As against the weight of analytical evidence for adulteration there stands the fact that the freezing-point was in each case normal, and that it would probably be beyond the skill of any dairyman to exactly adjust the freezing-point of the mixture of water and milk.

The attention of the Commissioner of Public Health was called to the peculiar facts of these two cases, and it was decided to investigate each case further.

It was found that the samples were from the same district, sample "A" being the mixed milk from six cows (Table II.), and "B" the mixed milk from two cows (Table III.).

Ten days after the legal samples were taken a food inspector familiar with the milking of cows attended in the afternoon at each dairy, saw each cow milked and "stripped," and measured and sampled the milk from each cow. The mixed milk in each herd was unfortunately not sampled, the results given for the mixed milk in Table II. being calculated from the individual yield.

TABLE III.—Herd B (Two Cows).

Cows.	1.	2.	Mixed milk.	Normal milk.
Yield	2 quarts	1.5 pint		
Total solids (per cent) .. ..	12.4	10.9	12.2	12.9
Fat (per cent) .. ..	4.0	3.8	4.0	4.0
Solids not fat (per cent) .. ..	8.4	7.1	8.2	8.9
Ash (per cent) .. ..	0.73	0.75	0.73	0.75
Nitrogen (per cent) .. ..	0.48	0.55	0.49	0.52
Chlorine in ash (per cent) .. ..	19.0	31.0	21.0	14.0
Chlorine calc. as NaCl (per cent) .. ..	31.3	51.1	34.6	23.0
Ratio—Ash : NaCl .. ..	3.1	1.9	2.8	4.6
Ratio—				
Ash × 100 : S.N.F. .. ..	8.7	10.5	8.9	8.3
Freezing-point (°C.) .. ..	-0.54	-0.54	-0.54	-0.555
Composition of solids not fat—				
Milk sugar (per cent) .. ..	54.8	40.0	52.9	52.8
Proteids (per cent) .. ..	36.4	49.1	38.1	37.8
Ash (per cent) .. ..	8.3	10.5	8.9	8.3

These results clearly show that the samples originally received, while below the legal minimum standard at which milk may be sold, had not been adulterated by the addition of added water.

The causes of the abnormality seem to have been similar in each case. In each, the cows got most of their food by grazing on the roads and vacant lands in their vicinity, and although the dairies were nearly two miles apart, the soil in the district is very poor, and the grass therefore probably poor in both quantity and quality. The food supply of the cows may therefore be safely taken as having been below normal.

Most of the cows were nearing the end of their period of lactation which is recorded as the period when "salty" milk is generally noted.

The inspector reported that cow No. 3 in Herd "A" was obviously sick.

The only cow giving milk which could be classed as normal was No. 2 of Herd "A."

The striking feature of these results is that from eight cows, seven of them being apparently in good health, only one cow gives milk which is normal. All the others are abnormal, particularly in the high proportion of chlorine present. But by far the most striking feature of these results is that although the milks vary so far from the normal in chemical composition, the freezing-point is practically normal throughout. The mammary glands of the cow, when unable to obtain the correct proportion of milk sugar, and other foodstuffs, adjust the osmotic pressure by adding an extra proportion of common salt from the blood.

It is evident from the amount of work which has been done by many workers in this direction, and the cases quoted give further proof, that certain organs of secretion work at definite osmotic pressures. This pressure is practically a constant, the variation being within extremely narrow limits. In the case of milk from the cow, the variation measured by the well-known freezing-point method lies between 0.54° C. and -0.56° C. This is the first case in many tests where we have found the freezing-point of an undoubtedly genuine milk to be higher than -0.55° C. Still an extremely rare variation of 0.01° C. from the normal is not serious in the use of the freezing-point as a factor in milk analysis.

It cannot be too strongly impressed on milk analysts that the mammary glands of the cow work almost entirely to a constant osmotic pressure, the constituents which produce the pressure varying according to the nature and amount of the food supply, and also according to the period of lactation. So far as it is at present known there is no other constant controlling factor. We found exactly the same osmotic pressure (measured by the freezing-point) in genuine milks which varied between 6.4 per cent solids not fat with 2.8 per cent fat and 9.7 per cent solids not fat with 5.6 per cent fat. The fact of the osmotic pressure being the one steady controlling factor in milk

production having been definitely established it is obviously absurd to continue judging the purity of a milk from the determination of factors which are variant and not constants. As the determination of the freezing-point gives an easy and accurate method of measuring the osmotic pressure, the freezing-point is obviously the constant factor which should be used in judging the purity of milk.

Fortunately in Australia we not only insist on purity of milk but on quality, and milk is not allowed to be sold from a cow which has to adjust the osmotic pressure with an extra proportion of common salt, or to keep itself warm in the absence of sufficient food or shelter by consuming fat which should have gone into the milk. It is therefore necessary to determine the ordinary factors, fat, solids not fat, &c., but these are not used and should not be used in determining the purity of the milk.

We put these analyses on record to once more emphasise the fact which we have previously noted (*Proceedings of the Australasian Association for the Advancement of Science*, xii., 160, and xiii., 88, and the *Proceedings of the Royal Society of Queensland*, xxiv., 165; see also *CHEMICAL NEWS*, 1914, vol. cx., pp. 275, 283), that the determination of the freezing-point of a milk is not only the most important factor to determine in milk analysis, but is the only factor which definitely settles whether or not water has been added to the milk, and is the only one which gives a close approximation to the proportion of water which has been added.

In the case of the two samples recorded the sellers, if judged by the old solids not fat standard, would certainly have been convicted for selling milk adulterated with water. As it was they were not prosecuted, but action was taken by the Health Department to prevent the further sale of these abnormal milks to the general public.

## THE SEPARATION OF TUNGSTEN FROM MOLYBDENUM.\*

By EDWARD ELLSWORTH MARBAKER.

WITH the extensive introduction of tungsten and molybdenum into industrial chemistry in the form of the special steels and the filament of the incandescent electric lamp, the importance of these metals has been greatly increased from the standpoint of the analytical chemist.

It is a well-known fact that molybdenum always accompanies tungsten in its ores, and it shows a marked tendency to remain with the tungsten throughout the process of manufacture. This amount of molybdenum, although small, interferes to a great extent with the determination of the tungsten, and hence one of the important problems in modern analysis is to devise a separation of the two metals which will be easy to carry out and also be of the highest accuracy. Up to the present time there have been suggested methods for the attainment of this end: Rose (Treadwell-Hall, *Analytical Chemistry*, II., 3rd ed., 1911, p. 296), Pechard (*Ibid.*, 295; *Compt. Rend.*, 1892, cxiv., 173), Smith and Reagenberg (*Journ. Am. Chem. Soc.*, 1900, xxii., 772; Treadwell Hall, 293), Ibbotson and Brearley (*CHEM. NEWS*, 1900, lxxxix., 13). In 1911, Mdivani (*Bull. Soc. Chem.*, [4] 1911, ix., 122) announced a new method for the determination of tungsten which was based on the observation of Anthon (Dammer, *Handbuch*, 1893, iii., 659; *Journ. Prakt. Chem.*, 1893, ix., 341) that when a tungstate solution is treated with a solution of stannous chloride, a yellow precipitate of normal tin tungstate,  $\text{SnWO}_4$ , is formed, which is changed to the blue oxide of tungsten,  $\text{W}_2\text{O}_5$ , on the addition of concentrated hydrochloric acid. Mdivani added to the tungstate solu-

tion a solution of stannous chloride in concentrated hydrochloric acid and then boiled for a few minutes. The blue oxide was precipitated and, after settling, was filtered off, washed with hot water, dried, ignited to tungsten trioxide and weighed as such.

### 1. An Effort to Reproduce the Results of Mdivani.

Mdivani made up a solution for analysis by dissolving 2 grms. of pure tungsten trioxide in strong ammonia and diluting to one litre. He treated 50 cc. of this solution, which contained 0.1 gm. of  $\text{WO}_3$ , with 20 cc. of a solution containing 50 grms. of crystallised stannous chloride in 200 cc. concentrated hydrochloric acid. The blue precipitate which was thrown down was boiled up for a few minutes and then allowed to settle, after which it was washed by decantation with hot distilled water and finally ignited and weighed as tungsten trioxide.

A weighed sample of pure tungstic acid, which had been prepared for the purpose of making ductile tungsten lamp filament, was treated with strong ammonia. The attack was not complete, showing that the purity of the substance was doubtful; but the solution was filtered and made up to one litre. Samples of this solution were analysed by evaporating to dryness three times with hydrochloric acid and nitric acid, baking at about  $120^\circ$  for fifteen minutes after each evaporation, then washing on to a filter with a hot ammonium nitrate solution, finally igniting and weighing. Fifty cc. of the solution were thus found to contain 0.1422 gm.  $\text{WO}_3$ . This value was obtained as the average of ten closely agreeing determinations.

A solution of stannous chloride was made according to the directions of Mdivani. Twenty cc. of the tin solution were added to 50 cc. of the ammonium tungstate solution, and the resulting blue precipitate was boiled for a few minutes and washed according to the directions of Mdivani. The pure water recommended for washing was found to be inadequate because it caused the formation of basic tin salts which could not be washed out, and hence gave rise to high results. This was easily remedied by washing the precipitates with a solution of hydrochloric acid made by adding 50 cc. of strong acid to a litre of boiling distilled water. The washed precipitates were thus entirely free from tin.

Four determinations resulted as follows—

$\text{WO}_3$ present	.. ..	0.1422 gm.
$\text{WO}_3$ found	.. ..	0.1392 "
		0.1386 "
		0.1390 "
		0.1387 "

To determine the cause of these low results, the filtrate from one of the determinations, which was perfectly clear and colourless, was evaporated to dryness. Blue oxide of tungsten separated. This showed that either the precipitation had not been complete or that the acid of the wash water had caused some of the oxide to pass into solution. Subsequent results indicated that the latter was not the case. The small amount of blue oxide was transferred to a filter and washed with the dilute acid until the filtrate gave no test for tin on the addition of ammonia. The filter and its contents were then ignited, but instead of obtaining a small amount of yellow tungsten trioxide, there was present a mixture of the yellow oxide and a white substance which proved to be tin oxide. This would indicate that a combination had taken place between the tin and the tungsten, because all of the tin had been washed out of the precipitate so far as the tests on the filtrate showed. In order to eliminate the small amount of tin, the residue was carefully treated with ammonium chloride, as recommended by Rammelsberg (*CHEM. NEWS*, 1864, ix., 25), which causes the tin to volatilise as stannic chloride, leaving the tungstic acid behind. The weight of this residue added to that of the main portion of the oxide brought the result into agreement with the theoretical.

\* From the Author's Ph D. Thesis, 1914, University of Philadelphia. Reprinted from the *Journal of the American Chemical Society*, xxvii., No. 1.

2. *The Action of Mdivani's Reagent on a Mixture of Ammonium Tungstate and Ammonium Molybdate.*

When stannous chloride was added to a solution of ammonium molybdate a brown precipitate appeared. This rapidly dissolved in the excess of the reagent, the solution assuming a characteristic orange colour, due to the reduction of the  $\text{MoO}_3$  to  $\text{Mo}_2\text{O}_3$ . This is very different from the reaction which takes place in the tungstate solution, hence it seemed possible to effect a separation.

A solution of molybdenum trioxide in ammonia was made up and analysed by the method of Chatard (CHEM. NEWS, 1871, xxiv., 175). Ten cc. of the solution were found to contain 0.1164 grm.  $\text{MoO}_3$ .

A solution containing 0.1164 grm.  $\text{MoO}_3$  and 0.1422 grm.  $\text{WO}_3$  was treated with 20 cc. of the tin solution and the resulting precipitate of  $\text{W}_2\text{O}_5$  handled as outlined before. It was washed with the acid wash water until the washings gave no test for tin. The filter and its contents were ignited and weighed. A fairly close value for the tungsten was obtained.

It was assumed at this point that the precipitate of tungstic acid contained no molybdenum, but a careful test was made to determine whether the filtrate containing the molybdenum contained any tungsten. This test was carried out as follows:—An excess of metallic zinc was added to the solution and the tin was precipitated as metal. The solution changed colour from orange to green. It was decanted from the tin, which was present in the form of a porous cake, and the tin washed several times with hot water. The clear green liquid was then evaporated on the hot plate, during which process the colour changed to brown again. When the bulk of the solution had been decreased to about 150 cc. a few drops of nitric acid were added. It rapidly became colourless, showing that the molybdenum had been oxidised to the form of molybdate. Ammonia was then added in great excess. The precipitate of zinc hydroxide which first appeared dissolved in excess, leaving a small precipitate of iron and tin hydroxides. This was filtered out and re-precipitated. The filtrate was added to the main solution and the whole treated with acid to the point of neutrality. A small amount (3—5 cc.) of acetic acid was then added, followed by an excess of lead acetate. A precipitate of lead molybdate was formed which, after settling, was filtered, washed with dilute acetic acid, ignited and weighed. This weight proved to be lower than the theoretical, but the loss could not be accounted for, although the precipitate of tin metal, the iron and tin precipitate, and the filtrate from the lead molybdate were all tested with zinc and sulphocyanide, but no evidence of molybdenum was observed.

The ignited residue of lead molybdate was then tested with hydrochloric acid, according to the method of separation suggested by Ibbotson and Brearley (CHEM. NEWS, 1900, lxxxi., 13). The solution of the residue was complete, but on dilution no tungstic acid separated out, thus showing that the molybdenum was not contaminated with any tungsten, and that, so far as the tungsten was concerned, the separation was complete.

It was found in other determinations, carried out in the same way, that the weight of the tungstic oxide was high, although all the tin had been removed by careful washing. The high results must then have been due to a small amount of molybdenum left in the tungsten. The precipitate of  $\text{W}_2\text{O}_5$  was dissolved in ammonia containing a little hydrogen peroxide and re-precipitated with a second portion of the tin solution. The precipitation at this point was never complete, because the filtrate had a blue colour. This was evaporated to dryness, the  $\text{W}_2\text{O}_5$  washed out and ignited with ammonium chloride and finally weighed. This weight was added to that of the main precipitate and the sum of the two gave a somewhat low result, due probably to unavoidable losses in the process of analysis.

A series of results follows—

Grm. $\text{WO}_3$ present.	Grm. $\text{WO}_3$ found.	Grm. $\text{WO}_3$ present.	Grm. $\text{WO}_3$ found.
0.1422	0.1426	0.1422	0.1412 (a)
0.1422	0.1414	0.1412	0.1405 (a)
0.1422	0.1420	0.1422	0.1414 (a)
0.1422	0.1434	0.1422	0.1434
0.1422	0.1432	0.1422	0.1428
0.1422	(a) 0.1401	0.1422	0.1415

Average 0.1422

(a) Re-precipitated.

These results indicate a possible separation of tungsten from molybdenum, although they are not particularly concordant. The molybdenum was not determined, because at the moment there was no method available for the separation of the molybdenum from extremely large amounts of tin.

3. *The Action of Mdivani's Reagent on a Mixture of Sodium Tungstate and Sodium Molybdate.*

Mdivani states in his paper that the quantitative precipitation of tungsten may be carried out as well in solutions of sodium and potassium tungstate and molybdate as in solutions of the ammonium salts.

The solution of sodium tungstate used was made from a portion of the salt which had been prepared by fusing together the theoretical amounts of pure  $\text{WO}_3$  and  $\text{Na}_2\text{CO}_3$  and crystallising the product. The solution contained 0.1489 grm.  $\text{WO}_3$  in each 10 cc. The solution of sodium molybdate was made by dissolving a sample of a salt, which had been made by Schuchardt, and afterwards re-crystallised several times. This solution contained 0.1200 grm.  $\text{MoO}_3$  in each 10 cc.

A sample of the tungstate solution was measured out and treated with the usual amount of Mdivani's reagent. The blue precipitate appeared and was filtered off. The filtrate was coloured blue, showing that the precipitation had not been complete. Several attempts were made to improve this precipitation by adding more reagent than usual and also by the addition of ammonium chloride, but without any favourable results.

A solution containing both tungstate and molybdate was then treated in the usual manner with the tin solution in order to determine the effect of the presence of sodium molybdate. The blue precipitate of  $\text{W}_2\text{O}_5$  came down well and was weighed after filtering and washing. The filtrate in this case was orange coloured, on account of the molybdenum present. A series of ten determinations was made and the results were so concordant and near the theoretical that it shows conclusively that for the amounts of tungstate and molybdate present a separation of tungsten and molybdenum can be effected by means of an acid stannous chloride solution. The results follow—

Grm. $\text{MoO}_3$ present.	Grm. $\text{WO}_3$ present.	Grm. $\text{WO}_3$ found.
0.1200	0.1489	0.1492
0.1200	0.1489	0.1489
0.1200	0.1489	0.1490
0.1200	0.1489	0.1486
0.1200	0.1489	0.1486
0.1200	0.1489	0.1489
0.1200	0.1489	0.1492
0.1200	0.1489	0.1486
0.1200	0.1489	0.1489
0.1200	0.1489	0.1489

As in the case or the separation of tungsten and molybdenum using the ammonium salts, the molybdenum was not determined.

The tungsten trioxide obtained in the foregoing analyses was tested for molybdenum by the method of Debray (*Comptes Rendus*, 1858, xli., 1101) by passing over it dry hydrogen chloride at a temperature of  $200^\circ$ . A slight sublimate of the compound  $\text{MoO}_3 \cdot 2\text{HCl}$  was formed, proving that a little molybdenum was present. On sub-

sequent analysis by the method of Chatard it was found that the molybdenum contained in the tungsten trioxide from six determinations amounted to less than 1 mgrm. of  $\text{MoO}_3$ .

The fact that the separation takes place so easily is so at variance with the usual experience of analysts of tungsten compounds that it seemed very remarkable that the molybdate actually aids the precipitation of the tungsten, as it will be remembered that the precipitation of  $\text{W}_2\text{O}_5$  from the tungstate alone is never complete. This was so peculiar that the effect of other salts on the precipitation was tried. The results of these tests were as follows—

Salt present.	Grm. $\text{WO}_3$ present.	Grm. $\text{WO}_3$ found.
0.1 grm. $\text{K}_2\text{SO}_4$ .. ..	0.1489	0.1481
0.1 grm. $\text{K}_2\text{SO}_4$ .. ..	0.1489	0.1488
0.2 grm. $\text{K}_2\text{CrO}_4$ .. ..	0.1415	0.1414
0.2 grm. $\text{NaCl}$ .. ..	0.1489	0.1487
0.2 grm. $\text{NaCl}$ .. ..	0.1489	0.1494

The filtrate from the tungsten in all of the foregoing determinations, except that containing chromium, was perfectly colourless. These results show that an accurate estimation of the tungsten in sodium tungstate can be made by the addition of any of the salts mentioned in the table.

In order to determine the availability of the method various amounts of sodium tungstate and sodium molybdate were taken. The results appear in the following table—

Grm. $\text{MoO}_3$ present	Grm. $\text{WO}_3$ present.	Grm. $\text{WO}_3$ found.
0.1200	0.0089	0.0089
0.1200	0.0149	0.0151
0.1200	0.0596	0.0592
0.1200	0.0900	0.0900
0.1200	0.1200	0.1200
0.1200	0.1788	0.1786
0.1200	0.2100	0.2101
0.1200	0.2400	0.2397
0.1200	0.2700	0.2700
0.1200	0.3000	0.2998
0.0121	0.1500	0.1496
0.0241	0.1500	0.1497
0.0482	0.1500	0.1500
0.0724	0.1500	0.1504
0.0965	0.1500	0.1499

#### 4. The Determination of the Molybdenum in the Filtrate from the Blue Oxide.

The filtrate from the tungsten contains all the molybdenum and a large amount of tin in the form of stannous and stannic chlorides. The tin was removed from the solution by means of metallic zinc, the filtrate was evaporated down to a small bulk, oxidised with nitric acid, and treated with an excess of ammonia. The zinc hydroxide which was thrown down dissolved in excess. The molybdenum was then precipitated by lead acetate after the solution had been almost neutralised with  $\text{HCl}$  and finally treated with a small excess of acetic acid. The precipitate of lead molybdate was allowed to settle, filtered, washed with hot dilute acetic acid, and finally weighed. In every case the result was low.

Since the foregoing procedure failed to solve the problem of determining the molybdenum, a careful review of literature was taken up in the hope that a method for determining molybdenum in a hydrochloric acid solution had been devised. Nothing of this nature was found in connection with any gravimetric method, but the discussion of the volumetric methods seemed to offer a means of solving the problem.

Randall (*Am. Journ. of Science*, [4], 1907, xxiv., 313) has shown that when a molybdate solution is passed through a Jones reductor and the reduced solution is caught in a ferric ammonium sulphate solution, decolorised by phosphoric acid, that the ferric iron oxidises the molybdenum, and the ferrous iron thus formed may be

titrated with standard potassium permanganate. This investigator proved that the molybdenum is completely reduced to the form of  $\text{Mo}_2\text{O}_3$ . Accordingly, a determination was carried out as follows: A portion of the sodium molybdate solution was measured out and treated with about 20 cc. of Mdivan's reagent. This gave rise to an orange coloured solution, to which were added about 5 grms. of pure 20-mesh zinc. The tin was deposited on the zinc as metal, and the green supernatant liquid was poured off, the tin washed with hot water, and then the solution and washings were heated to about  $60^\circ$ .

The reductor flask was charged with 20 cc. of the ferric alum solution and 20 cc. of the "titrating solution." (This consisted of 90 grms. manganous sulphate, 650 cc. distilled water, 175 cc. syrupy phosphoric acid, and 175 cc. concentrated sulphuric acid). Fifty cc. of dilute hydrochloric acid (2.5 per cent by vol. of the concentrated acid heated to  $60^\circ$ ) were passed through the reductor, followed by the solution containing the molybdenum, and then 150 cc. of the warm acid and finally 150 cc. of hot distilled water.

The flask was removed from the reductor and the titration was carried out in the usual way with the permanganate (standardised against ferrous ammonium sulphate and also oxalic acid) solution. The molybdenum solution before entering the reductor is green, while in the reductor the reduction is completed, although there is no noticeable change in colour. When the green solution enters the ferric solution the colour changes to red. This red solution is titrated with permanganate, but the red colour offers no obstacle, because, as the permanganate is added, this colour disappears, and toward the end of the titration the colour of the solution is a faint bluish green in which the end-point is very easily seen. The end-point has to be taken very quickly, as it is not at all permanent. However, the titration is one which is very easily carried out.

A number of such determinations were made with the following results—

Grm. $\text{MoO}_3$ present.	Grm. $\text{MoO}_3$ found.	Grm. $\text{MoO}_3$ present.	Grm. $\text{MoO}_3$ found.
0.1500	0.1505	0.1350	0.1354
0.1500	0.1505	0.1635	0.1632
0.1470	0.1476	0.1200	0.1198
0.1500	0.1498	0.1050	0.1051
0.1500	0.1498	0.1800	0.1801

They show that the separation of tin from molybdenum by means of metallic zinc is quantitative and that the method may be used to determine the molybdenum in the filtrate from the tungsten in the method of separation under consideration.

#### 5. The Separation of Tungsten from Molybdenum.

The two processes outlined in the third and fourth sections of this paper were combined, and both constituents of the mixture of sodium tungstate and molybdate were determined.

The separation worked very well with quantities up to and including 0.3000 grm. of each constituent. More than this amount gave rise to high results unless an inordinate amount of time was consumed in washing out the molybdenum from the tungsten. The high results can be more quickly corrected by treating the ignited residue of  $\text{WO}_3$  with as many cc. of concentrated hydrochloric acid as there are centigrams. of the residue and boiling for a few minutes. Then this may be diluted with three times its volume of hot water and allowed to settle. This process removes the contaminating molybdenum and leaves the tungsten pure. The filtrate containing the small amount of molybdenum is of course added to the main molybdenum solution. There seem to be no limits to the applicability of the molybdenum titration. When large amounts of molybdenum were present it was found advisable to make up to 250 cc. and work with portions o

50 cc. each. The latter method proved to be a great factor in reducing the time of the determination.

When moderate samples are used the whole process, involving the determination of both the constituents, can be carried out in about three hours. The greater part of this time is consumed in washing the tungsten precipitate and in evaporating the filtrate containing the molybdenum to a bulk which may be easily handled.

The results of ten complete separations follow—

Grm. WO <sub>3</sub> present.	Grm. MoO <sub>3</sub> present.	Grm. WO <sub>3</sub> found.	Grm. MoO <sub>3</sub> found.
0.1005	0.1005	0.1001	0.1010
0.1500	0.1500	0.1496	0.1498
0.2000	0.2000	0.2004	0.1995
0.2520	0.2505	0.2526	0.2499
0.3015	0.3000	0.3016	0.2997
0.3500	0.3500	0.3508	0.3502
0.4005	0.4005	0.4008	0.3995
0.4500	0.4500	0.4508	0.4495
0.4995	0.4995	0.4999	0.4994
0.3000	0.3000	0.3000	0.2996

### Summary.

Tungsten and molybdenum, in the form of their sodium salts, may be quickly and easily separated, the course of analysis being as follows—

To a boiling solution containing the tungstate and molybdate of sodium in appropriate amounts add the tin solution (50 grms. SnCl<sub>4</sub>·2H<sub>2</sub>O dissolved in 200 cc. concentrated HCl) in the proportion of 20 cc. for each 0.15 gm. WO<sub>3</sub> present. This amount of the reagent should be carefully regulated, because less will not effect a complete separation, and more will be correspondingly harder to handle in the determination of the molybdenum. The dilution of the solution for analysis should be kept between 60 cc. and 300 cc., depending on the amount of tungsten present. After boiling a few minutes allow the blue precipitate of W<sub>2</sub>O<sub>5</sub> to settle and then pour the orange supernatant liquid through a filter. Wash the precipitate thoroughly by decantation with hot 5 per cent hydrochloric acid until the washings give no test for molybdenum by the zinc and thiocyanate method. Bring the precipitate on the filter and allow to drain. If the amount of precipitate is small the filter may be ignited wet, but if the amount be large it is better to heat it until the greater part of the water has been driven off. Place the filter in a porcelain crucible and ignite gently to WO<sub>3</sub>. Cool in a desiccator and weigh.

The filtrate and wash water are united and the whole evaporated to a small bulk. If the amount of tungsten and molybdenum taken has been large, cool and dilute to 250 cc. and use aliquot portions of 50 cc. To this solution add from 5—10 grms. of 20-mesh zinc. The tin will come out as metal. Pour off the green solutions when the precipitation of the tin is complete (this takes about ten minutes), and wash the cake of tin several times with hot water. Unite the filtrate and wash water and heat to 60°. Pass through the reductor in the order named, 50 cc. dilute HCl (containing 2.5 per cent by volume of the strong acid,) the solution containing the molybdenum, 150 cc. 2.5 per cent (vol. conc. HCl), and finally 150 cc. hot distilled water. These pass into the flask of the reductor, which has been previously charged with 20 cc. 10 per cent ferric ammonium sulphate and 20 cc. of the "titrating solution." This solution is next titrated with approximately 0.1 N potassium permanganate and the amount required calculated to MoO<sub>3</sub>.

If it is desired to determine the amount of tungsten in a sodium tungstate solution, add to that solution a quantity of sodium chloride solution, and proceed as when molybdenum is present.

A fairly accurate separation of tungsten and molybdenum may be effected when they are present as ammonium salts, but the method is not to be highly recommended.

## ON THE ACTION OF LEAD, COPPER, TIN, NICKEL, ZINC, AND ALUMINIUM ON WATER.

By Dr. W. P. JORISSEN, The University, Leiden, Holland

### 1. Introduction

In conformity with a request on the part of the Chemical Section of the Eleventh International Pharmaceutical Congress, I have readily undertaken to report on the above-named subject. In a literal sense this would imply a paper about the action of the elements lead, copper, tin, nickel, zinc, and aluminium on pure water, but, however important this action may be from a scientific point of view, it is of much more practical importance to know the action that takes place when the above-named metals—pure or not—are brought into contact with water, such as is found in nature and practice, *i.e.*, water containing air and a number of other substances. This, however, materially extends the subject under discussion.

That iron is not included in the above heading may seem strange at first sight, as this metal takes a prominent position in life. Considering, however, that two important treatises on the corrosion of iron and its technical alloys have lately appeared (Note 1), the exclusion of this metal will be understood, notwithstanding the fact that after their publication some interesting papers on this subject have seen the light (Note 2).

Lead has been included in spite of the report issued by Messrs. H. W. Woudstra and C. J. Snijf at the Conference held in this country on the Chemistry of Food-Stuffs. But their papers dealt principally with the action of lead on drinking waters and the hygienic side of the question (Note 3).

To have let copper drop out would have been more according to expectation, as two years ago in the Institute of Metals an extensive report on the corrosion of copper and some of its alloys at the hand of G. D. Bengough came out (Note 4).

With a view to the request to limit the length of the reports as much as possible, I have tried to render in a concise manner the principal facts on the domain to be considered. I have, however, made mention of such publications as would enable the reader, if necessary, to become acquainted with the principal literature on the subject. Moreover, I have not taken into account the hygienic side of the problem, as I do not feel competent to judge.

Before entering into a detailed discussion of the corrosion by air and water of the various above-named metals, it is necessary to make some general remarks.

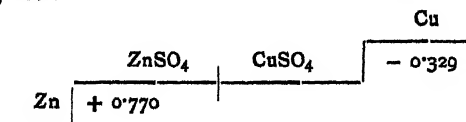
### 2. General Remarks.

If the potential differences are determined between metals (placed in normal solutions of their ions) and a hydrogen electrode, the following table (series of electrochemical potentials) is obtained, in which a lower placed metal possesses a higher potential than a higher placed one.

	Volt.
Magnesium .. .. .	+1.482
Aluminium .. .. .	+1.276
Manganese .. .. .	+1.075
Zinc .. .. .	+0.770
Cadmium .. .. .	+0.420
Iron .. .. .	+0.311
Cobalt .. .. .	+0.232
Nickel .. .. .	+0.248
Tin .. .. .	+0.192
Lead .. .. .	+0.151
Hydrogen .. .. .	0
Copper .. .. .	-0.329
Bismuth .. .. .	-0.391
Antimony .. .. .	-0.466
Mercury .. .. .	-0.753
Silver .. .. .	-0.771
Platinum .. .. .	-0.863
Gold .. .. .	-1.079



About the + and - symbols the following remark may be made:—In passing from copper to a normal solution of copper sulphate, the potential sinks 0.329 volt, in passing from zinc to a normal solution of zinc sulphate it rises 0.770 volt.



If one were to start from the liquid and pass on to the metal the symbols would be reversed. Hence the symbols would also occur reverted in the above table. It need hardly be said that this has no influence on the calculation of potential differences. In case of alteration of the concentration of the solutions the potential differences are also changed. Thus, e.g., the potential difference copper-copper sulphate solution will be raised when the concentration of the solution is raised; in the case of zinc-zinc sulphate solution the potential difference will be lowered under similar circumstances. As a rule, however, the differences are not very marked. If totally different solutions are taken, the potential difference metal-solution will undergo a greater change, but the order of the metals in the table will generally remain the same (Note 5).

Thus the potential difference between zinc and copper, which in normal solutions of their ions amounts to 1.1 volt (0.770 + 0.329) has been found to be about 1 volt in drinking water and distilled water. That between iron and copper, according to the above table, 0.673 volt, is in a 3 per cent solution of chloride of sodium about 0.4 volt, in distilled water about 0.5 volt (Note 6).

The potential difference between a metal and a solution of one of its salts may be explained as follows:—Take for instance zinc placed in a solution of zinc sulphate and copper in a solution of copper sulphate. When the solutions are brought into contact by means of a porous wall or a syphon and the metals by a wire, we observe that zinc passes into solution (emits ions) and copper is deposited on the copper rod (i.e., copper ions lose their charge); SO<sub>4</sub>-ions pass through the porous wall or the syphon. When those metals are placed disconnectedly in solutions of their salts, we have simply to assume that also in that case the zinc begins by sending out some ions and that on the copper some copper ions will be discharged. Then the zinc must, in consequence of sending out positively charged particles, take a negative charge, whilst the copper receives a positive one from the copper ions. The two processes of emitting and receiving will soon stop. For instantly in the layer between metal and solution an "electric double-layer" is formed. With zinc it consists of zinc ions on the side of the liquid and of an equivalent quantity of negative electricity on the side of the metal. With copper it is formed by attracted SO<sub>4</sub>-ions at the side of the liquid and by an equivalent quantity of positive electricity at the side of the metal (Note 7). The arising potential difference opposes the sending out of zinc ions, respectively the discharging of copper ions. Soon its value becomes so considerable as to prevent the emitting of zinc ions and the discharge of copper ions (Note 8).

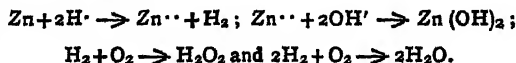
If the metals and solutions are connected, an electric current is flowing, the zinc is enabled to send out ions continuously, whilst copper will be deposited all the time on the copper. A similar action takes place when zinc is immersed in a solution of copper sulphate. Zinc ions are emitted; the negatively charged zinc attracts copper ions. If some of these are discharged on the zinc a galvanic cell is formed, in which the solving process of the zinc and that of depositing copper can proceed without interruption.

When we immerse zinc in a solution of sulphuric acid we expect an analogous result, i.e., the dissolving of zinc and the escaping of hydrogen, which is indeed observed in

the case of crude zinc. With pure zinc no, or only a slight, liberation of hydrogen is perceptible, which, however, takes place energetically whenever the metal is brought into contact with rods of carbon, copper, or silver, for instance, but in this case the gas escapes at those rods. It has been found that for the electrolytic liberation of hydrogen on other metals than platinised platinum a higher E.M.F. is required, which, according to W. A. Caspari (Note 9), amounts to 0.15 volt for silver, 0.21 volt for nickel, 0.23 volt for copper, 0.48 volt for cadmium, 0.53 volt for tin, 0.64 volt for lead, 0.70 volt for zinc in acid containing zinc, 0.78 volt for mercury. Mott (Note 10) gives the following list of overvoltages:—Tin 0.55, lead 0.50, antimony 0.45, bismuth 0.45, gold 0.20, silver 0.15, platinum 0.15, iron 0.10, brass 0.14 volt.

These metals appears to be less able than platinised platinum to counteract the resulting polarisation by causing hydrogen to escape. With the exception of mercury, the hydrogen can escape more easily from the other above-named metals than from zinc. Hence the liberation of hydrogen on the copper or silver which we bring into contact with the zinc. Hence its liberation on zinc which contains impurities such as, for instance, lead and carbon. Then we have the galvanic cell: zinc, zinc salt solution, acid, hydrogen (occluded in lead). We can calculate the E.M.F. of this cell by subtracting the overvoltage of lead (0.64 volt) from the E.M.F. of the cell: zinc, zinc salt solution, acid, hydrogen (in platinised platinum), 0.77 volt. We then find a small positive value, so that the contact with lead will hasten the solution of the zinc. However, the overvoltage of mercury (0.78 volt) being greater than the E.M.F. of the above cell, the contact with mercury does not accelerate; thus a partly amalgamated rod of pure zinc will not show any perceptible liberation of hydrogen (Note 11).

**Oxidation of Metals.**—If we immerse zinc in distilled water, we have to do with another liquid in which H-ions occur. The concentration of these amounts to only about  $1 \times 10^{-7}$  grms. per litre. The zinc sends out Zn-ions, as appears from the charge which it takes. H-ions will therefore be attracted. With pure zinc, however, we do not expect a perceptible liberation of hydrogen, even less than when immersing it in a solution of sulphuric acid, where the concentration of H-ions is so much more considerable. If oxygen is present, however, it may oxidise the hydrogen to water and peroxide of hydrogen (Note 12) on the surface of the zinc, new Zn-ions being formed.



The peroxide may further act upon the zinc, new Zn-ions being formed.

As regards metals placed in the series much lower than hydrogen, no displacement of hydrogen is to be expected.

From the conduct, however, of metals which are to be found very near to each other in the series it may be concluded what will happen to those metals which stand close to hydrogen. Take, for instance, lead and tin of which one immediately follows the other. In solutions of the sulphates and chlorides of those metals an equilibrium will establish itself between the two metals, in which their salts will share with finite concentrations (Note 13).

Now, copper is to be found just below hydrogen. Thus, in immersing this metal in dilute sulphuric acid, we may assume the equilibrium  $\text{Cu} + 2\text{H}^+ \rightleftharpoons \text{Cu}^{++} + \text{H}_2$ , which, however, lies almost entirely on the left side of the equation. A considerable increase of the H-ions, however, will shift the equilibrium to the right; hence the accelerating influence of an increasing concentration of the acid on the corrosion of copper by air in the presence of dilute sulphuric acid (Note 14). This corrosion again takes place through the oxidation of the liberated hydrogen on the face of the copper (Note 15).

## Notes.

1. A. S. Cushman and H. A. Gardener, "The Corrosion and Preservation of Iron and Steel," New York, 1910; J. Newton Friend, "The Corrosion of Iron and Steel," London, 1911. See also in O. F. Hudson's "Iron and Steel" (London, 1913) the chapter written by G. D. Bengough on Corrosion, and e.g., O. Kröhnke, "Ueber das Verhalten von Guss- und Schmiederohren in Wasser, Salzlösungen, and Säuren," München, 1911.
2. W. R. Dunstan and J. R. Hill, *Journ. Chem. Soc.*, 1911, xcix., 1836; B. Lambert, *Ibid.*, 1912, ci., 2056.
3. *Chem. Weekbl.*, ix., 447-457, 1913-1917; see also P. A. Meerburg's paper, *Chem. Weekbl.*, ix., 494-497, and the discussion on Messrs. Woudstra and Smit's report, *Ibid.*, ix., 1917-1922.
4. *Journ. of the Institute of Metals*, 1911, v., 28-88; see also the discussion on this report, *Ibid.*, pp. 89-114, and some papers which appeared afterwards. J. T. Corner, "Some Practical Experience with Corrosion of Metals," *Ibid.*, v., 115-126; P. T. Brühl, "The Corrosion of Brass," *Ibid.*, 1911, vi., 279-304; A. Philip, "Contributions to the History of Corrosion," *Ibid.*, 1912, vii., 50-69.
5. For the change of places between iron and tin, which are to be found close together in the table, and for others, see, e.g., W. P. Jorissen, "On Galvanic Action," *Jaarverslag Technol. Gezelsch.*, Delft, 1913, 1911-12, pp. 13-14. Diegel, *Marine-Rundschauf*, 1898, ix., 1485, mentions the following series for some metals placed in sea-water:—Zinc, aluminium or iron, tin, copper. For the change of places between aluminium and zinc see this Report, *prox.*
6. E. Heyn and O. Bauer, *Mittel. Konigl. Materialpruf. amt Gros-Lichterfelde West*, 1908, xxvi., 21.
7. The presence of a layer of ions around the charged metal has been proved by W. Palmaer, *Zeit. Phys. Chem.*, 1898, xxv., 265.
8. For simplicity's sake, Nernst's "electrolytic solution pressure" and his formula for the calculation of the E.M.F. of a galvanic cell have been omitted. See his "Theoretische Chemie," 1913.
9. *Zeit. Phys. Chem.*, 1899, xxx., 93. See for the way in which this cathodic overvoltage is influenced by the physical condition of the metal and the part played by overvoltage in assisting or preventing the solution of a metal (J. I. Crabtree, *Journ. Soc. Chem. Ind.*, 1913, xxxii., 521).
10. Cited by Hambeuchen, *Journ. Inst. of Metals*, 1911, i., 321.
11. That totally amalgamated zinc does not dissolve is due to the high overvoltage of the mercury, the alloy assuming the overvoltage of the external metal; compare J. I. Crabtree, *Journ. Soc. Chem. Ind.*, 1913, xxxii., 521.
12. As regards the formation of hydrogen peroxide during the oxidation of zinc, see M. Traube, *Ber.*, xv., 664; 1893, xxvii., 1472; compare W. B. Jorissen, *Zeit. Phys. Chem.*, 1897, xxii., 49.
13. O. Sackur, *Arch. a. d. Kais. Gesundh. ante*, 1904, xx., 512. From a solution of lead acetate the lead is almost wholly precipitated by tin; from a solution of stannous nitrate the tin is almost wholly precipitated by lead.
14. O. Sackur, *Ibid.*, 1906, xxiii., 287.
15. See for the formation of hydrogen peroxide M. Traube, *Ber.*, 1882, xv., 664; 1883, xvi., 130.

(To be continued).

## ENGLISH FILTER PAPER.

It is well known that hitherto the supply of high-class filter-paper for analytical work has been left almost entirely to the Continental manufacturer.

The War has changed many things, and at a time when so much is being said and written about capturing the "enemy's trade," it is a pleasure to find that in this particular branch of manufacture at least one English firm of repute has set to work quietly and systematically to meet the need. Messrs. W. and R. Balston, Ltd., the makers of the well-known "Whatman Drawing Paper," have through their agents forwarded samples of their first production, a filter-paper of very excellent quality. We have made some careful tests, and find that, as stated by the makers, it is quite equal to the best German material. Ordinary filtration is very rapid, and finely divided barium sulphate filters clear and bright. Compared with the well-known S and S 595 it passes cold water much more rapidly, and the ash content marked on each packet is very small. The price is the same as the German material.

Messrs. Balston, in placing this paper upon the market, draw attention to the fact that in this their first production they have had to prepare a paper to compare favourably with one that has been the result of many years' experience by their foreign competitors, and we can sincerely congratulate them upon their success. The firm is now engaged upon the preparation of hydrochloric and hydrofluoric treated paper, and we shall look forward with interest to the result. Messrs. Balston's agents are H. Reeve Angel and Co., 15, New Bridge Street, E.C., and the papers can be obtained from the usual trade houses.

## NOTICES OF BOOKS.

*A Text-book of Inorganic Chemistry.* Volume I. Part I. *An Introduction to Modern Inorganic Chemistry.* By J. NEWTON FRIEND, D.Sc. (Birmingham), Ph.D. (Würz.), H. F. V. LITTLE, B.Sc. (London), A.R.C.S., D.I.C., and W. E. S. TURNER, D.Sc. (London), M.Sc. (Birmingham). Part II. *The Inert Gases.* By H. VINCENT A. BRISCOE, B.Sc. (London), A.R.C.S., D.I.C. London: Charles Griffin and Co., Ltd. 1914.

THIS series of text books on inorganic chemistry will play a valuable part in the education of students of chemistry of the present generation, who will find it admirable, both as regards the matter contained in it and the abundant references to more detailed works. The writing of the first volume, dealing with the general principles of the science and the inert gases, undoubtedly presented the greatest difficulties, which have been very successfully surmounted. The fundamental laws of the science, the general properties of elements and compounds, molecular weight determinations, types of chemical change, &c., are clearly discussed, and the text is thoroughly up-to-date; for example, some account is given of Moseley's recent work on the X-ray spectra of the elements, and allusion is made to the Quantum theory. It seems a pity that Sir J. J. Thomson's method of positive ray analysis is not described in outline, but on the whole the authors' choice of material is excellent. In the second part a clear account is given of the chemistry of the inert gases, and some debatable questions and speculations relating to them are described in detail.

*The Rare Earths: their Occurrence, Chemistry, and Technology.* By S. I. LEVY, B.A. (Cantab.), B.Sc. (London), A.I.C. London: Edward Arnold. 1915.

THE attention paid to the rare earths in English literature, and by English teachers of inorganic chemistry, is perhaps hardly commensurate with their growing importance

Institution of Petroleum Technologists.—Lord Fisher of Kilverstone and Vice Admiral Sir Edmond J. W. Slade have been elected honorary members of the institution.

and the amount of work which is being done upon them, and hence this book on the subject will be welcomed by a large number of workers and students. It gives a general but at the same time fairly detailed account of the occurrence, chemistry, and technology of the rare earths, zirconium and thorium being included as well as titanium, on account of its great interest and its use in volumetric work. The third part of the book, dealing with technology, is particularly valuable, and this branch of the subject is in every way admirably treated.

*Outlines of Organic Chemistry.* By F. J. MOORE, Ph.D. Second Edition. New York: John Wiley and Sons Inc. London: Chapman and Hall, Ltd., 1914.

THIS book, the second edition of which has been thoroughly revised, is intended more particularly for the use of the general student of science, and hence it is not difficult to find omissions in it which might, perhaps, be regarded as detracting from its value from the point of view of the specialist. On the other hand, much attention is paid to subjects of practical importance and to the applications of organic substances. Thus the synthesis of rubber is treated fairly fully, and compounds, such as starch, sugar, linseed oil, &c., which are of importance in every-day life, are described in more detail than is usual in works on elementary organic chemistry. A chapter on the chemistry of vital processes will be found specially useful by students of biology.

*The "Wellcome" Photographic Exposure Record and Diary,* 1915. London: Burroughs, Wellcome, and Co.

THIS photographic exposure record will be found very useful by all photographers, both amateur and professional. It is provided with a diary and tables, showing the relative exposures required by various brands of plates and films. It also contains much miscellaneous photographic information, and blank tables ruled for records of negative and positive exposures, in addition to many recipes and directions for developing, fixing, intensifying, and reducing, &c.

*Practical Handbook for Beet-Sugar Chemists.* By WERNER MOELLER-KRAUSE. Easton, Pa.: The Chemical Publishing Co. 1914.

IT seems hardly probable that this book will find extensive use in England, for it suffers from all the common defects of a handbook which is merely a condensation of larger works, and presents very few compensating advantages. The descriptions of analyses have been abridged to such an extent that only the experienced worker could glean much from them, and many details which are absolutely indispensable from the beginner's point of view are altogether omitted. Thus, although there is a lettered diagram of a polariscope no explanation of it is given, nor is the reader provided with any directions for using the instrument. On the other hand, the student is not supposed to know the correct way to read the level of a liquid in a graduated flask. A fairly lengthy account is given of the process of the manufacture of sugar, and also some rather scrappy descriptions of the analysis of water, limestone, fuels, gases, &c.

*Year Book of Pharmacy.* London: J. and A. Churchill. 1914.

THIS year-book contains short abstracts of all the papers on pharmacy and materia medica which have appeared in British and foreign journals between July 1, 1913, and June 30, 1914. These abstracts are well classified and indexed, and will be of great use to pharmacists. A list of subjects suggested for research is added, and attention is called to the fact that a special fund exists to defray expenses connected with research work. Particulars may be obtained from the Executive Committee of the British Pharmaceutical Conference. The year-book also contains a full account of the Conference at Chester in July, 1914, at which some exceedingly useful and practical papers were read and discussed.

## CORRESPONDENCE.

To the Editor of the Chemical News.

SIR,—I enclose a copy of a paper on actinium and ionium, recently presented to the Royal Society of New South Wales. It is practically a summary of a paper read before the recent meeting of the British Association in Sydney.

I had an opportunity of going into the question of the recovery and isolation of actinium with Sir E. Rutherford during his visit, and he considers that its isolation should be quite practicable in the conditions under which I am working.—I am, &c.,

S. RADCLIFF.

Dunheved, Alexandra Street, Hunters' Hill, N.S.W.,  
Nov. 19, 1914.

### ON THE RECOVERY OF ACTINIUM AND IONIUM FROM THE OLARY ORES.

A general account of the methods devised for extracting radium from the interesting ore complex occurring at Olary, S. Australia, has already been given; the present communication deals with the recovery of the ionium and actinium.

Both ionium and actinium possess many of the properties of the rare earths, and separate out along with these in the course of treatment. It is necessary, therefore, to investigate the distribution of the rare earths in the various residues and precipitates produced in treating the ore, and to examine these chemically, and also by means of the electroscope.

*Ionium.*—As ionium appears to be chemically inseparable from thorium, the activity of the ionium preparation that can be separated from a given ore depends on the ratio of the uranium to the thorium in it.

The chemistry of thorium has been very fully worked out, and in order to obtain an active ionium preparation from an ore, all that is necessary is to extract the thorium and purify it by any of the well-known methods. The uranium thorium ratio for the Olary ore is about 100:1; it is possible, therefore, to obtain from it ionium preparations of considerable activity.

*Actinium.*—Our knowledge of the chemistry of actinium is very imperfect. None of its salts have yet been prepared in a state approaching purity, and methods for its complete isolation remain to be devised; the progress of the separation can of course be followed by means of the electroscope. Unfortunately, actinium preparations frequently show little or no activity initially, and it is necessary to keep them for some weeks in order to observe the characteristic rise of the activity with time.

The uranium concentrates as received for treatment contain between three and four per cent of rare earths, the mixture having the composition:—

	Per cent.
Thorium oxide .. .. .	0.32
Cerium oxide .. .. .	27.60
La and Dy oxide .. .. .	46.60
Yttrium oxide .. .. .	25.30

These earths distribute themselves in three of the works' products.

They are found:—

- In the hydroxides of the elements of the iron group, which are precipitated by carbonate of soda during the extraction of the uranium.
- In the uranium oxide recovered.
- In the mixture of impure sulphates of lead, barium, and radium recovered in the course of the extraction of the radium.

The uranium oxide contains only traces of rare earths, and as these are only very feebly radio-active, they have not been examined in detail.

The hydroxides (a) when washed and dried contain about 5 per cent. of a mixture of rare earths of the composition:—

	Per cent.
Thorium oxide .. ..	7.5
Cerium oxide .. ..	34.7
La and Dy oxide .. ..	26.3
Yttrium oxide .. ..	31.5

These rare earths appear to be actinium free.

The sulphate mixture (c) contains about 3 per cent of rare earths of the composition:—

	Per cent.
Thorium oxide .. ..	13.2
Cerium oxide .. ..	44.0
La and Dy oxide .. ..	42.6
Yttrium oxide .. ..	trace

The activity of these rare earths increases at about the rate expected from the presence of actinium, and almost the whole of the actinium in the ore appears to be carried down with the precipitated lead and barium sulphates.

This is in accord with the observations of Debiegne, who states that actinium can be removed from a solution by precipitating barium as sulphate in it.

As 10 tons of concentrates yield only 40 kilos. of sulphates the concentration of the actinium is very considerable. The sulphates, which have the composition—

	Per cent.
Lead sulphate .. ..	69.24
Barium sulphate .. ..	12.50
Ferric oxide .. ..	2.15
Silica .. ..	10.82
Titanic oxide .. ..	3.00
Rare earths .. ..	3.00

are treated as follows:—

1. They are fused in an iron crucible with excess of caustic soda, containing some carbonate of soda. The melt is extracted repeatedly with hot water; this removes the greater part of the lead.

2. The insoluble residue is digested under a steam pressure of 90 lbs. with an excess of carbonate of soda.

3. The carbonate residue, after washing, is treated with dilute hydrogen chloride and the solution evaporated to dryness. The residue is taken up with water, and the silica filtered off.

4. The solution is saturated with gaseous hydrogen chloride and the radium and barium quantitatively precipitated.

The solution contains the actiniferous rare earths. It is evaporated to dryness to expel the excess of hydrogen chloride, and the residue is then treated for the separation of the actinium.

It is hoped that ultimately sufficient material will be available to allow of pure salts of actinium being prepared.

The determination of both the atomic weight and the period of actinium is much to be desired, as a knowledge of these two constants would fix the position of actinium and its products in the disintegration series of the radioactive elements.

## MISCELLANEOUS.

**Institute of Chemistry.—Pass List, January (1915) Examinations.**—The results of the examinations of the Institute of Chemistry recently held in London have now been published. Of four candidates who presented themselves for the Intermediate Examination two passed: G. T. Bray and E. G. Macintyre, B.Sc. (Glasgow). Of thirteen candidates who presented themselves for the Final (A.I.C.) Examination five passed: In the Branch of Mineral Chemistry—R. L. Amore and E. G. G. Wheeler; in the Branch of Organic Chemistry—W. J. S. Naunton, M.A. (Cantab.), B.Sc. (London), and H. Shulman, B.Sc. (London); in the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—W. S. Clark.

**Society of Public Analysts.**—The Annual General Meeting of the Society will be held on Wednesday,

February 3, at the Chemical Society's Rooms, Piccadilly, W., at 8 p.m. The accounts for the year will be presented, the President will deliver his Annual Address, and the election of Officers and Council for the ensuing term will take place. The appointment of Auditors will also take place. The Ordinary Monthly Meeting of the Society will be held immediately following the annual general meeting, when the following papers will be read: "Note on the Determination of Sulphates in Flour," by G. D. Elsdon, R.Sc., A.I.C.; "General Principles governing the complete Analysis of Minerals and Ores," by W. R. Schoeller, Ph.D. *Dinner Club.*—Members of the Society and their friends will meet to dine at the Hotel Previtali, Arundell Street, Piccadilly Circus, at 6.15 p.m., when it is hoped that as many as possible will be present.

**Chemical Industry.**—Those who are interested in the welfare of the chemical industries will be glad to learn that the formation of a powerful Central Committee, representing chemical manufacturers and scientific societies, has been decided upon, and that a meeting of all concerned has been convened, and will meet next week to consider the present situation. A preliminary meeting has already been held. The meeting will be held at the offices of the Institute of Industry and Commerce, Exhibition Buildings, Aldwych Site, Strand, W.C. Chemical manufacturers who are interested can obtain permission to attend the meeting by making application to the Secretary at the above address. The fact that our most eminent men of science are leading the movement, and are seeking the co-operation of the chemical manufacturers, should ensure a successful issue to the movement.

**Society of Chemical Industry (London Section).**—The next meeting of the Section will be held at the Chemical Society's Rooms, Burlington House, Piccadilly, on Monday February 1, at 8 p.m. As already announced in the *Journal of the Society of Chemical Industry*, specimens of chemicals and apparatus will be shown which have been mainly produced abroad hitherto, but are now being manufactured in this country. Mr. J. J. Eastick will move the following resolution:—

That in the opinion of this Meeting representing the London Section of the Society of Chemical Industry, the Council of the Society should petition the Government to take such steps as will tend to the permanent production and refining within the Empire of sugar sufficient for the Empire's consumption.

## MEETINGS FOR THE WEEK.

- MONDAY, Feb. 1st.**—Royal Institution, 5. General Meeting. Society of Chemical Industry, 8. Royal Society of Arts, 8. (Cantor Lecture). "Oils, their Production and Manufacture," by Dr. F. Mollwo Perkin.
- TUESDAY, 2nd.**—Royal Institution, 3. "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S. Royal Society of Arts, 4.30. "Sugar and the War," by E. R. Davison.
- WEDNESDAY, 3rd.**—Royal Society of Arts, 8. "Imperial Industrial Development after the War," by O. C. Beale. Society of Public Analysts, 8. "Determination of Sulphates in Flour," by G. D. Elsdon. "General Principles governing the complete Analysis of Minerals and Ores," by W. R. Schoeller.
- THURSDAY, 4th.**—Royal Institution, 5. "Modern Theories and Methods in Medicine," by H. G. Plimmer, F.R.S. Royal Society, "Discontinuous Fluid Motion past a Bent Plane, with special reference to Aeroplanes," by G. I. Bryan and K. Jones. "The Spectra of Ordinary Lead and Lead of Radioactive Origin," by T. R. Merton. "Viscosity of the Vapour of Iodine," by A. O. Rankine. Chemical, 8.30. "Metallic Compounds of Cobalt and Nickel," by S. U. Pickering. "Preparation of Dinitro-dichloro-methane by simultaneous Nitration and Chlorination of Acetone," by J. N. Rakshit. "Azotisation by Chloroamine," by M. O. Forster.
- FRIDAY, 5th.**—Royal Institution, 9. "Science and Industrial Problems," by Dr. A. W. Crossley, F.R.S.
- SATURDAY, 6th.**—Royal Institution, 3. "Music to Untrained Listeners," by H. Walford Davies, Mus.Doc.

# THE CHEMICAL NEWS.

Vol. CXI., No. 2880.

## NITROGEN AND CHLORINE IN RAIN AND SNOW.

(SECOND PAPER).

By WILLIAM K KNOX.

WIESNER (CHEMICAL NEWS, 1914, cix., 85) determined the nitrogen and chlorine in the different precipitations at Mount Vernon, Iowa, during the year 1912-1913. We

have continued the work during the year 1913-1914, and collected 43 samples, 36 of rain and 7 of snow, from October 4, 1913, to June 12, 1914. The samples were collected in porcelain-lined pans, 20 inches in diameter, in an open space near the centre of the village. The population is about 2400 and there are no manufactures in the community.

The snowfall during the period amounted to 11.5 inches, equivalent to 0.95 inch of rain. The rainfall was 17.75 inches, a total of 18.7 inches of rain, which is above the normal for this section. The heaviest fall occurred on June 4, when the precipitation was 4.5 inches in a few hours. This contained a large amount of the various substances, as will be seen from the accompanying tables.

The chlorine was quite constant, showing 10.6 parts per million. In calculating the results we considered that an inch of rainfall on an acre weighs 226.875 pounds.

TABLE I.—Parts per Million.

Date.	Rainfall.	Chlorine.	Nitrates	Nitrites	Free ammonia.	Alb. ammoniz.	Sulphate.
October..	4	10.6	0.30	0.001	1.12	1.37	
	7	10.6	0.32	0.0012	0.355	0.659	
	10	10.6	0.25	0.002	0.112	0.197	
	16	10.6	0.25	0.004	0.230	0.041	
	19	10.6	0.40	0.010	1.31	0.131	
	26	10.6	0.30	0.001	0.230	0.065	
November	28	10.6	0.40	0.002	0.032	0.461	
	7	10.6	1.40	0.002	2.635	1.547	
	26-28	10.6	0.70	0.002	1.31	1.976	
	30	10.6	0.35	0.003	1.120	0.922	
December	6	10.6	0.45	0.004	1.120	0.922	
January..	18	10.6	1.50	0.001	0.092	1.976	
	25	7.1	0.25	0.004	0.092	0.131	
	28	10.6	0.35	Trace	0.922	0.131	
February	6	12.4	0.35	0.001	0.922	0.131	
	15	10.6	0.50	0.001	0.65	0.16	
March ..	16	10.6	0.60	0.015	0.092	0.263	
	6	7.1	0.41	0.001	0.230	0.296	
	7	7.1	0.12	0.002	No test	No test	
	21	24.85	0.48	0.001	0.196	1.31	
	26	12.4	0.50	0.002	1.12	0.296	
	27	2.5	0.55	0.001	2.96	5.25	
	28	0.96	0.20	0.001	1.96	0.40	
	29	0.35	0.32	0.0015	0.165	0.112	
	31	10.6	0.45	0.001	0.296	0.131	
April . .	11	10.6	0.35	0.001	0.296	0.40	
	18	10.6	0.40	Trace	0.23	0.13	
	18	10.6	0.35	0.002	0.196	0.29	
	24	10.6	0.42	0.001	0.29	1.12	
	26	10.6	0.36	0.0015	0.32	1.65	
	28	10.6	0.25	0.001	0.23	0.59	0.0186
May . . .	3	10.6	0.40	0.001	1.12	1.96	0.063
	7	10.6	0.60	0.001	1.66	1.96	0.0126
	7	10.6	0.30	0.001	No test	No test	
	10	10.6	1.20	0.0015	No test	No test	
	11	10.6	0.35	0.001	0.52	0.65	
	21	10.6	0.30	0.001	0.922	0.06	
	24	10.6	0.40	0.002	0.98	0.196	
	26	10.6	0.35	0.001	No test	No test	
	27	10.6	0.28	0.001	0.922	0.197	
June . . .	4	7.1	0.25	0.001	0.98	0.197	

TABLE II.—The Amounts per Acre.

Date.	Precipitation.	Chlorine.	Nitrates.	Nitrites.	Free ammonia	Alb. ammon	Sulphate
October. . .	4	0.60122	0.001694	0.000056469	0.06352	0.07736	
	7	0.12024	0.003629	0.000013611	0.00402	0.00749	
	10	0.60122	0.014138	0.0000112938	0.00632	0.00706	
	16	1.81864	0.042351	0.000677628	0.03896	0.00644	
	19	0.12024	0.004537	0.000013437	0.03754	0.00375	
	26	1.20253	0.034031	0.0000113437	0.02609	0.00737	
	28	0.045374	0.000223874	0.000362	0.05229	0.05229	
November . .	7	0.12024	0.015880	0.000022387	0.00362	0.05229	
	26-28	0.12024	0.008000	0.000022387	0.01485	0.02341	
	30	1.20252	0.019802	0.000340341	0.12704	0.10458	



TABLE II.—The Amounts per Acre (continued).

Date.	Precipitation.	Chlorine.	Nitrates.	Nitrites.	Free ammonia.	Alb. ammon.	Sulphate.
December ..	6 0.25 (rain)	0.60122	0.025411	0.000225876	0.06324	0.05206	
January. ..	18 4.00 (snow)	0.59857	0.084703	0.000056469	0.00519	0.11158	
	25 1.00 (snow)	0.1314	0.000047	0.0000567	0.02079	0.02972	
	28 0.6 (rain)	1.1991	0.039593	0.0004525	0.12652	0.01769	
February ..	6 1.0 (snow)	0.02325	0.006617	Trace	0.17402	0.02406	
	15 1.0 (snow)	0.03235	0.009453	0.0001890	0.04743	0.03630	
	16 0.5 (rain)	1.2025	0.001134	0.0068002	0.01043	0.03360	
March ..	6 0.5 (snow)	0.0671	0.004159	0.0001417	0.02084	0.02796	
	7 1.0 (snow)	0.1342	0.002268	0.0000190	No tests made		
	21 3.0 (snow)	1.4066	0.027225	0.0001134	0.01111	0.07450	
	26 1.0 (rain)	2.8122	0.0113437	0.0002268	0.2540	0.0671	
	27 0.5 (rain)	0.6012	0.062390	0.0002268	0.03357	0.5955	
	28 1.0 (rain)	2.722	0.045363	0.0002268	0.4446	0.0906	
	31 0.5 (rain)	1.1343	0.051046	0.0001134	0.3357	0.0148	
April ..	11 0.25 (rain)	0.5671	0.019851	0.0000567	0.0111	0.2268	
	18 0.25 (rain)	—	0.022687	0.0000567	0.0130	0.0073	
	18 0.25 (rain)	—	0.019851	Trace	0.0111	0.0164	
	24 0.25 (rain)	1.5671	0.023821	0.0001134	0.0164	0.0063	
	26 0.75 (rain)	1.7015	0.061257	0.0001701	0.0544	0.2806	
	28 0.5 (rain)	1.1343	0.028359	0.0001601	0.0260	0.0669	0.0638
May ..	3 0.5 (rain and hail)	1.1343	0.045374	0.0001134	0.1270	0.2223	0.0218
	7 0.25 (rain)	1.5671	0.034031	0.0001134	0.0935	0.1111	0.0436
	7 0.1 (rain)	0.2268	0.006806	0.0000226	No tests made		
	10 0.75 (rain)	1.7015	0.0404188	0.0001701			
	11 0.25 (rain)	0.05671	0.019851	0.0000567	0.0291	0.0357	None
	21 0.2 (rain)	0.4537	0.013612	0.0004537	0.0413	0.0027	"
	24 0.25 (rain)	0.5671	0.022684	0.0005671	0.5558	0.1111	"
	26 0.1 (rain)	0.2268	0.007940	0.0004526	No tests made		
	27 0.5 (rain)	1.1343	0.031762	0.0001134	0.1145	0.0233	"
June ..	4 4.5 (rain)	7.2486	0.0350265	0.0009209	0.9506	0.1962	"
Total ..		36.8488	1.542451	0.0129669	3.6933	2.7946	0.1292

On April 28 we made our first test for sulphate, and found it also in two subsequent precipitations. Later in the season no trace of sulphate was found, indicating that it comes from the sulphur in the coal.

Our thanks are due to Dr. N. Knight for his assistance in this work.

Cornell College, December 19, 1911.

## THE PERCHLORIC METHOD OF DETERMINING POTASSIUM AS APPLIED TO WATER ANALYSIS.

By CLARENCE SCHOLL.

POTASSIUM is determined gravimetrically as potassium chloroplatinate ( $K_2PtCl_6$ ), as potassium cobaltinitrite ( $K_2Co(NO_2)_6$ ), and as potassium perchlorate ( $KClO_4$ ).

The potassium chloroplatinate method is most commonly used. It is accurate, but there are difficulties because of the solubility of the salt in alcohol, the non-uniformity of the precipitate, the loss by ignition, and the cost of material. The cost of chloroplatinic acid equivalent to 1 gram of potassium in the precipitate,  $K_2PtCl_6$ , amounts to 4.90 dols. While this material can be recovered, the cost of recovery is considerable.

The determination as potassium cobaltinitrite in its present form is not satisfactory (H. B. McDonnell, Bur. Chem. Bull. 162, 19, 1912). The results are unreliable.

The potassium perchlorate method, more commonly called the Wense-Caspari method (W. Wense, *Zell. Angew. Chem.*, 1891, iv., 691; 1892, v., 233; R. Caspari, *Ibid.*, 1893, vi., 68), has been applied to the analysis of fertilisers and similar material containing alkalis, alkaline earths, iron, aluminium, magnesium, and phosphates. The chief difficulty in this method has been the obtaining of the perchloric acid. The danger of preparing the pure acid, as was attempted, is very great. For this reason the

method has not been available to many chemists. Recently a 20 per cent solution at 3.00 dols. a kilo., a 30 per cent solution at 4.80 dols. a kilo., and even stronger solutions of perchloric acid have been placed on the market.

The quantity of perchloric acid necessary to combine with 1 gram of potassium costs 3.8 cents. The cost of an equivalent amount of chloroplatinic acid is 4.90 dols. The cost of perchloric acid in the perchlorate method is not only lower than the cost of platinum in the chloroplatinate method, but is much lower than the cost of recovering the platinum. The precipitate  $KClO_4$  is of constant composition, its solubility in 96 per cent alcohol containing 0.2 per cent  $HClO_4$  is almost zero, and the loss by ignition is eliminated. The fertiliser chemists of Germany have tested the method (*Landw. Ver. Sta.*, 1903, lix., 313; 1907, lxvii., 145), and have obtained such accurate results that they have placed it on an equal basis with the chloroplatinate method by adopting it as an official method (*Fifth Internat. Congr. of Appl. Chem.*, 1903, i., 216; 1903, iv., 940).

In this method the sulphates are precipitated in a slightly acid solution. This solution of chlorides is then treated with an excess of perchloric acid (1.5 times that required to combine with all bases present), and evaporated with constant stirring until white fumes appear. A small amount of water is then added, and again evaporated with stirring. This is continued until all volatile acids are absent. The perchloric acid lost by volatilisation is replaced from time to time. The precipitate,  $KClO_4$ , obtained is washed with 95 per cent alcohol immediately before drying.

The author has modified this method as follows:—Precipitate the sulphates in a strong hydrochloric acid solution, avoiding a large excess of barium chloride. Evaporate the resulting solution with only a slight excess of perchloric acid without stirring. Dissolve the residue, and again evaporate with perchloric acid. Wash the precipitate only with alcohol containing 0.2 per cent perchloric acid before drying.

The revised method as applied to the determination of potassium in water is as follows:—Evaporate an aliquot portion of the water to about 150 cc. Acidify with 10 cc. of concentrated hydrochloric acid, and heat to boiling. To the boiling solution add drop by drop (avoiding a large excess), a 10 per cent solution of barium chloride until all the sulphates are precipitated. Boil for fifteen minutes, and then filter. If no precipitate forms, filtration may be omitted.

Evaporate the filtrate to dryness. Heat until all the ammonium salts are driven off. Dissolve in 20 cc. of hot water, and add a quantity of a 20 per cent solution of perchloric acid, slightly in excess of that required to combine with nearly all bases present. One cc. of perchloric acid is equivalent to 90 mgrms. of potassium, K. Evaporate to dryness. Add 10 cc. of hot water and a small amount of perchloric acid. Again evaporate to dryness. If white fumes do not appear, take up with 10 cc. of water, add more perchloric acid, and evaporate to dryness. Repeat until white fumes do appear. Take up with 25 cc. of 96 to 97 per cent alcohol, containing 0.2 per cent perchloric acid (1 cc. of 20 per cent  $\text{HClO}_4$  per 100 cc. of 97 to 98 per cent alcohol). Break up the residue with a stirring rod. Decant the supernatant liquid through a Gooch crucible containing a matt that has been washed with 0.2 per cent perchloric acid in alcohol. If there is an unusually large precipitate, dissolve it in hot water, and repeat the evaporation with perchloric acid. (Large quantities of barium chloride are difficult to change to the perchlorate). Wash once by decantation with 0.2 per cent perchloric acid in alcohol, and transfer the precipitate to the crucible. Wash several times with 0.2 per cent perchloric acid in alcohol. Dry the crucible in an oven at 120–130° for an hour. Remove, cool, and weigh. The increase in the weight of the crucible is  $\text{KClO}_4$ . (In using the Gooch crucibles, do not disturb the matt after analysis. Dissolve the potassium perchlorate with hot water, leaving the matt intact. Using the crucible repeatedly in this manner eliminates the errors due to the action of perchloric acid on fresh asbestos).

If both sodium and potassium are to be determined, obtain the combined chlorides by the usual methods, and estimate the potassium as potassium perchlorate as described, omitting the precipitation of the sulphates with barium chloride.

It is of advantage to evaporate to dryness with only a slight excess of perchloric acid, and to repeat the process a second, and possibly third time, in order to insure the removal of nearly all volatile acids, and in order to make stirring while evaporating unnecessary.

The recommendation of 97 per cent alcohol for washing is due to the solubility of potassium perchlorate in alcoholic solutions of perchloric acid containing 95 per cent or less alcohol. The difference between the efficiency of 97 per cent and 100 per cent alcohol is immaterial.

It is undesirable to wash the crucible with ether or alcohol just before drying. A slight amount of potassium perchlorate would be dissolved. Dry as much as possible with air suction, and then dry in an oven. The small amount of perchloric acid left in the asbestos will be volatilised without causing any error, especially if the same asbestos matt is used repeatedly.

A series of analyses was first made using only potassium chloride (see Table I.). This potassium chloride, the purest of a well-known firm, was dried at 180° for several hours before using. A standard solution was then prepared, and definite amounts measured out with a standardised pipette.

Since the amount of potassium found agreed with the amount taken, a second series was analysed, using comparatively large amounts of sodium chloride in addition to the potassium (see Table II.).

The variations are small, and lie within the limits of experimental error. The largest is -0.9 mgrm. The average for the 15 analyses is 0.2 mgrm. less than the theoretical amount. The balance used is not capable of

TABLE I.—Analyses of Solutions containing only Potassium Chloride.

No.	Potassium added, grm.	$\text{KClO}_4$ obtained, grm.	Potassium obtained, grm.	Error, grm.
1.	0.0050	0.0174	0.0049	-0.0001
2.	0.0100	0.0353	0.0100	—
3.	0.0150	0.0530	0.0150	—
4.	0.0200	0.0701	0.0198	-0.0002
5.	0.0300	0.1049	0.0296	-0.0004
6.	0.0350	0.1241	0.0350	—
7.	0.0500	0.1769	0.0499	-0.0001

TABLE II.—Analysis of Solutions containing Large Quantities of Sodium Chloride.

No.	Potassium added, Grm.	Sodium chloride in solution, Grm.	$\text{KClO}_4$ obtained, Grm.	Potassium obtained, Grm.	Error.	
					Grm.	Per cent
1.	0.0050	0.0500	0.0181	0.0051	+0.0001	+2.0
2.	0.0100	0.1000	0.0350	0.0099	-0.0001	-1.0
3.	0.0200	0.2000	0.0712	0.0201	+0.0001	+0.50
4.	0.0300	0.3000	0.1073	0.0302	+0.0002	+0.66
5.	0.0400	0.4000	0.1423	0.0401	+0.0001	+0.25
6.	0.0500	0.5000	0.1783	0.0503	+0.0003	+0.60
7.	0.0600	0.6000	0.2129	0.0600	—	—
8.	0.0700	0.7000	0.2471	0.0697	-0.0003	-0.40
9.	0.0800	0.8000	0.2830	0.0799	-0.0001	-0.11
10.	0.1000	1.0000	0.3534	0.0997	-0.0003	-0.30
11.	0.2000	1.0000	0.7090	0.2001	+0.0001	+0.05
12.	0.3000	1.0000	1.0626	0.2999	-0.0001	-0.03
13.	0.4000	1.0000	1.4171	0.3999	-0.0001	-0.03
14.	0.5000	1.0000	1.7686	0.4991	-0.0009	-0.18
15.	1.0000	1.0000	3.5438	1.0000	—	—

TABLE III.—Analyses of Waters of High Mineral Content.

No.	Mineral content.	Potassium added, grm.	$\text{KClO}_4$ obtained, grm.	Potassium obtained, grm.	Error, grm.	Per cent
1.	0.0500	0.6000	0.1757	0.0496	-0.0004	-0.80
2.	0.1500	0.6000	0.5301	0.1497	-0.0003	-0.20
3.	0.2500	0.6000	0.8887	0.2508	+0.0008	+0.32
4.	0.3000	0.6000	1.0612	0.2995	-0.0005	-0.17
5.	0.3500	0.6000	1.2378	0.3493	-0.0007	-0.20

TABLE IV.—Analyses of Highly Mineralised Water containing Phosphate.

1.	0.0500	0.7000	0.1784	0.0503	+0.0003	+0.60
2.	0.1000	0.7000	0.3540	0.0999	-0.0001	-0.10
3.	0.1500	0.7000	0.5323	0.1502	+0.0002	+0.13
4.	0.2500	0.7000	0.8867	0.2501	+0.0001	+0.04
5.	0.3500	0.7000	1.2385	0.3494	-0.0006	-0.17

weighing less than 0.1 of a mgrm. The error in percentage is large with small quantities (amounting to as much as 2.0 per cent). Increasing the quantity of potassium decreases the error in percentage.

An artificial mineralised water was then made by adding the following constituents to distilled water:— $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{NO}_3$ . The insoluble constituents were dissolved with a small amount of hydrochloric acid. Portions of this solution containing 0.1 grm. of each substance ( $\text{CaCO}_3$  and  $\text{MgCO}_3$  now being present as  $\text{CaCl}_2$  and  $\text{MgCl}_2$  respectively), were measured out. Known amounts of potassium were then added to each portion, and determined without removing any of the ions. The results are shown in Table III. In this series most of the errors, although not large, are minus in character.

To each of several portions of the same artificial water 0.1 grm. of  $\text{Na}_3\text{PO}_4$  was added, and the potassium determined as above, with results as shown in Table IV.

Though sodium phosphate is insoluble in alcohol, it does not produce an error in the determination of potassium (see Table IV.). When sodium phosphate is evaporated with  $\text{HClO}_4$ , the following reaction takes place:— $\text{Na}_3\text{PO}_4 + 3\text{HClO}_4 = 3\text{NaClO}_4 + \text{H}_3\text{PO}_4$ . Sodium

perchlorate and phosphoric acid are soluble in alcohol, and do not cause an error in the determination of potassium.

The sulphate and ammonium ions were found to produce an error, but the error caused by the sulphate was not equivalent to all the sulphate ion that was present. It is necessary to remove all of the ammonium salts and most of the sulphates.

#### Summary.

The method of determining potassium as the perchlorate is accurate.

Sulphate and ammonium ions produce an error, and must be removed. The sulphate is precipitated with barium chloride in a strongly acid solution avoiding a large excess. The ammonium salts are expelled by heating.

The phosphate ion does not produce an error, and need not be removed.

The solution containing chlorides should be evaporated to dryness with a slight excess of perchloric acid, without stirring.

The precipitate should be washed only with alcohol containing 0.2 per cent perchloric acid.

The time of making an analysis is short, the manipulations are simple, and the cost is almost negligible.

The method can be recommended for use in water analyses and in other analytical work where the content of potassium is desired.—*Journal of the American Chemical Society*, xxxvi., No. 10.

## SOME RAPID METHODS FOR GLASS ANALYSIS.

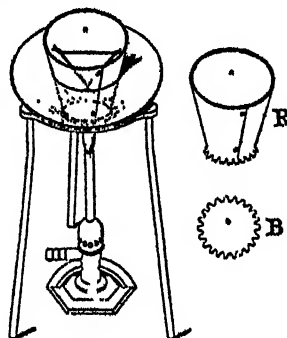
By E. C. SULLIVAN and W. C. TAYLOR.

SOME convenient methods which we have developed for the routine analyses of glasses may be capable of further application, and we therefore desire to bring them to the attention of others. Our original procedure for a complete analysis was to determine the alkalis by the J. Lawrence Smith method and the other bases and silica by fusion with soda. In some cases we were able to make use of the decomposition of glass by hydrofluoric and sulphuric acids. After some experimenting we found that we could use oxalic acid in place of sulphuric to decompose the fluorides. The oxalates can in turn be decomposed by heat, so that no bases or acids are introduced to interfere with the determination of the glass constituents. By this method the complete analysis of a glass may be finished in one day.

This method was developed for the analysis of a large number of glasses of the same type. These contained silica, lead, soda, and potash in varying proportions, with small amounts of iron, alumina, manganese, lime, and magnesia as impurities. For these glasses the following method was used:—One gm. of finely-powdered glass is placed in a platinum crucible of about 40 cc. capacity, moistened with water, 2 grms. of  $H_2C_2O_4$  crystals added and enough 48 per cent HF to fill the crucible half full. This is evaporated to dryness on a radiator, the temperature of which is just high enough to expel the excess of oxalic acid. When all the acid has been expelled the crucible is cooled and the evaporation repeated twice more with oxalic acid and water. The amount of oxalic acid used is about 5 grms. in all. It was necessary to know the amount used as a blank showed 0.0012 gm. of alkali chlorides from this source. After the third evaporation, when all the excess of oxalic acid is expelled, the remaining oxalates are taken up with hot water, allowed to cool and filtered. The residue which, in the case of the glasses mentioned, consists of  $PbC_2O_4$  only, with trace of  $CaC_2O_4$ , may be titrated directly with  $KMnO_4$  or dissolved in dilute  $HNO_3$  and determined as sulphate. The filtrate from the  $PbC_2O_4$  is evaporated to dryness in a platinum dish and then heated over a free flame until oxalates are

decomposed. The carbonates are then taken up with water and HCl and the mixture is evaporated to dryness to remove the small amount of  $SiO_2$ . The salts are taken up with a few drops of HCl and hot water, a few drops of bromine water added, then a little ammonia, and the solution is boiled. The precipitate of hydroxides of iron, aluminium, and manganese is filtered off, ignited and weighed. The filtrate is divided into two equal portions. To one are added  $NH_4OH$  and  $(NH_4)_2HPO_4$ , which precipitate a small amount of magnesia—about 1 mg. This is calculated to chloride and deducted from weight of NaCl, KCl. The other half is evaporated to dryness, ammonia salts expelled by heat, and the chlorides weighed. The  $MgCl_2$  found and alkali from blank determination on all reagents are subtracted and the  $K_2O$  determined by the platinum chloride method and  $Na_2O$  by difference.

(NOTE.—The radiator used was made up from a description by W. F. Hillebrand in *Bulletin* No. 422, U.S. Geol. Survey, p. 31, and is described here as it has considerable influence on the success of the method. R is of sheet iron, aluminium, or nickel, 6 to 7 cm. high, 8 cm. wide at top and 5 cm. at bottom. The base is may be of



iron, nickel, or platinum but not of aluminium, which will not stand the temperature of the direct flame. R is attached to B by turning the cogs of B up and over those of R. A platinum triangle should be inserted about 4 cm. from the base. An aluminium ring with an opening slightly larger than the underlying crucible should be placed over the radiator to hasten evaporation).

The following table will show some of the results obtained on weight of alkali chlorides from 1 gm. sample—

Glass No.	J. L. Smith method.	Oxalate.
	Grm.	Grm.
1.	0.1170	0.1175
	0.1168	0.1162
	0.1176	0.1169
		0.1163
2.	0.1177	0.1199
3.	0.1196	0.1198
4.	0.1290	0.1291
5.	0.1168	0.1160

On the separation of soda and potash the oxalate method averages about 0.15 per cent lower in  $K_2O$  and correspondingly higher in  $Na_2O$ . The lead determination by the oxalate method expressed in per cent  $PbO$  compares as follows—

Soda fusion.	Oxalate.
21.00	21.22
21.13	21.15
	21.30
	21.18

The combined weights of iron, alumina, and manganese amount to from 1 to 1.5 per cent and average from 0.2 to

0.3 per cent lower by the oxalate method than by the soda fusion. The amounts of CaO and MgO are in the neighbourhood of 0.1 per cent, and are slightly lower by the oxalate method where determined, though these determinations were usually omitted. We have used this method since on a large number of similar samples and have found it satisfactory for glasses of this type.

In applying this method to other glasses the procedure following the three evaporations must of course be varied. The first step is to separate the soluble and insoluble oxalates. From there on the procedure may vary according to what elements are present. The oxalates we have worked with group themselves as follows—

*Insoluble.*

Lead	Copper 2	Magnesium 2
Calcium	Cobalt 2	
Zinc	Nickel 2	
Cadmium 1	Barium 2	

*Soluble.*

Sodium	Manganese 3
Potassium	Iron 4
Aluminium	Arsenic
Chromium	Antimony 5

1. Almost quantitative; in presence of zinc traces present with soluble oxalates.
2. Though mostly insoluble, these elements must be looked for with the soluble oxalates unless particular precautions are taken to have conditions right to render the oxalates insoluble. Presence of other elements also affects the solubility of these oxalates.
3. Manganese up to 2 per cent gave no test for the element with the insoluble oxalates, but a glass containing 6 per cent MnO showed nearly half this amount as an insoluble oxalate.
4. Does not occur with insoluble oxalates except in zinc glasses when a small amount is found with the zinc.
5. Normally soluble but has been found with insoluble oxalates when these were heated too strongly.

Arsenic or antimony, if present, should be removed from the soluble oxalates with  $H_2S$  before the oxalates are decomposed. This necessitates acidifying with HCl, which must be expelled before decomposing the remaining oxalates; otherwise alkali chlorides are volatilised. The insoluble oxalates are in general dissolved in dilute HCl and separations made as in any mixture of chlorides. Borates do not interfere with the analysis. A number of analyses of glasses and silicates of other types are given to show results obtained by this method. The figures given are the difference between the oxalate method from the soda fusion and J. Lawrence Smith method. They are expressed as + when oxalate method is higher and — when lower.

	A	B	C	D	E	F
$Na_2O$ ..	-0.08	+0.26	-0.16	-0.11	+0.18	+0.14
$K_2O$ ..	-0.06	+0.00	+0.10	+0.00	-0.08	-0.04
CaO ..	-0.22	-0.05	—	-0.05	—	—
$Al_2O_3 \cdot Fe_2O_3$	+0.04	-0.08	—	+0.00	+0.03	-0.04
ZnO ..	—	+0.13	+0.07	-0.30	+0.04	—

- A. An ordinary soda lime glass.  
B. A soda lime, zinc borosilicate.  
C. A soda potash zinc glass.  
D. A soda zinc borosilicate.  
E. A soda potash zinc glass.  
F. A soda alumina borosilicate.

The presence of more than 3 per cent alumina causes difficulty, owing to its interfering with the expulsion of fluorine by oxalic acid. Except the lead glass all those containing  $Al_2O_3$  gave a test for fluorine in the soluble oxalates, and the amount of such fluorine was greater for high  $Al_2O_3$  content than for low.

Felspar gave very low results for alkali. A sample yielding 0.1246 grm. of alkali chlorides by the J. Lawrence Smith method gave 0.0909 grm. by the oxalate method. This was increased to 0.1102 grm. by reprecipitation of the alumina and to 0.1230 grm. by a second reprecipitation. With several alumina glasses low results were obtained on both  $Al_2O_3$  and alkali, while with other glasses either  $Al_2O_3$  was low and alkali high or alkali was low and alumina high. From the data at hand it seems as if both alkali and  $Al_2O_3$  were apt to be lost at some stages of the analysis, but so far our results are not consistent, probably due to the variation in temperature in different analyses. In some we get conditions favourable for a loss of alkali, in some for a loss of  $Al_2O_3$ , and sometimes for both. We have, with great care in heating, obtained only slightly low results where both  $Al_2O_3$  and  $Na_2O$  were very high as in cryolite. The loss therefore probably can be prevented.

Boric oxide tends to alleviate the difficulty caused by alumina and it does not in any way interfere with later determinations. Borosilicates with up to 5 per cent  $Al_2O_3$  give fairly good results. One showed 4.82 per cent  $Al_2O_3$  and 0.1010 grm. alkali chlorides by regular methods and 4.93 per cent  $Al_2O_3$  and 0.1027 grm. alkali chlorides by the oxalate method. The results on glass G mentioned in the table are not very good, however. With glasses not containing  $B_2O_3$  the addition of boric acid before evaporation with HF and  $H_2C_2O_4$  decreased the fluorine content of the soluble oxalates and also gave higher results for  $Al_2O_3$  and alkali without showing any  $B_2O_3$  present with the alkali.

From the results so far we do not feel confidence in the method for such glasses as show undecomposed silicofluorides, for while accurate determinations may be obtained with special precautions the method has no advantages under such conditions. For glasses which do not contain much  $Al_2O_3$  the method seems well adapted, especially for the analysis of a series of glasses of very nearly the same composition. We have also found it convenient for the rapid determination of  $As_2O_3$  or  $Sb_2O_3$  in glass.

*Determination of Boric Acid.*

In the analysis of borosilicate glasses we have found that for the determination of boric oxide the method described by Wherry (*Journ. Am. Chem. Soc.*, 1908, xxx., 1687) is very useful—

“Fuse the sample with about 3 grms. of  $Na_2CO_3$  for fifteen minutes. Take up with 20 to 30 cc. of dilute HCl, adding a few drops of  $HNO_3$  to oxidise ferrous iron. Place in a 250 cc. round-bottomed flask, heat nearly to boiling, and add dry precipitated  $CaCO_3$  in moderate excess. Connect with a return condenser and boil vigorously for about ten minutes. Filter out the precipitate through a small Buchner funnel, washing several times with hot water, but keeping the total volume of liquid below 100 cc. Return the filtrate to the flask, add a pinch of  $CaCO_3$  and again heat to boiling; then connect with a filter pump, through a splash trap, and continue suction until the boiling has nearly ceased. Cool to the ordinary temperature, filter if the precipitate has a red colour from iron, add four or five drops of phenolphthalein, and run in slowly N/10 NaOH solution until the liquid is strongly pink in colour. Introduce about 1 grm. of mannite and shake, whereupon the pink colour will disappear. Add NaOH to end reaction, then another grm. of mannite and if necessary more alkali until a permanent pink colour is obtained.”

The method was first tried by fusing 0.5 grm. sand and 0.2 grm. boric acid with 3 grm. soda. The melted mass was taken up with water and 7 cc. conc. HCl added after transfer to a 250 cc. flask. The method was then followed as described above except titration was made with  $Ba(OH)_2$ . The  $B_2O_3$  content came from 2 to 10 per cent low, due to retention of  $B_2O_3$  by the precipitate from  $CaCO_3$ . By using suction in filtering and washing this

precipitate practically 100 per cent of the  $B_2O_3$  introduced was recovered. For 0.25 grm.  $B_2O_3 = 12.40$  Ba(OH) $_2$  we used 12.35 and 12.40 cc. As iron and alumina are rarely present in large amounts in glass, and as the time of the soda fusion with glass can be cut to a few minutes, the method seemed quite readily adaptable.

The first glass tried was a soda alumina borosilicate which, from analysis, showed a possible  $B_2O_3$  content of 10.40 per cent by difference. Three determinations by Wherry's method showed 10.72, 10.57, 10.67 per cent  $B_2O_3$ , or an average of 10.64 per cent. A soda borosilicate containing a small amount of BaO and  $Sb_2O_3$  showed 25.57 per cent  $B_2O_3$  by Wherry's method and 25.75 per cent by difference. Other glasses of same type showed—

Per cent $B_2O_3$ by titration.	Per cent $B_2O_3$ by difference
25.10	25.12
12.71	12.15
17.57	17.51
14.90	15.01

With a zinc borosilicate very unsatisfactory results were obtained, the  $B_2O_3$  content by titration running from 4 to 9 per cent when only 2 per cent was present. Several mixtures of ZnO and sand with a known amount of  $B_2O_3$  were run through by Wherry's method, and results for  $B_2O_3$  were always high even after very long boiling. Solutions of  $ZnCl_2$  and borax were boiled with  $CaCO_3$  for varying lengths of time and using slight excess and large excess of  $CaCO_3$ , and zinc was always found in the filtrate from the  $CaCO_3$  precipitate. CaO was substituted for  $CaCO_3$  but with no better success.  $Na_2CO_3$  completely removed the zinc from solution, and by a double precipitation, using first  $Na_2CO_3$  and then  $CaCO_3$ , we obtained 0.0360, 0.0361, and 0.0365 grm.  $B_2O_3$  when the theoretical amount was 0.0365 grm. PbO was found to cause the same trouble as ZnO and the same modification of the method gave satisfactory results. We have been able to use the modified method on a large number of glasses with satisfactory results.

The modified method then is as follows:—Fuse 0.5 grm. of glass with 3 grm.  $Na_2CO_3$  for one or two minutes after mass is liquid. Take up with 20 to 30 cc. of hot water and when the melt is entirely decomposed filter out any insoluble oxides. After washing, transfer filtrate and washings to a 250 cc. round-bottomed flask, add about 7 cc. concentrated HCl, heat nearly to boiling, and add dry precipitated  $CaCO_3$  in moderate excess. From here on the method is as given by Wherry except that we used Ba(OH) $_2$  instead of NaOH. It is also advisable to use suction for filtering the  $CaCO_3$  precipitate.—*Journal of Industrial and Engineering Chemistry*, vi., No. 11.

## SOME ASPECTS OF INDUSTRIAL CHEMISTRY.\*

By L. H. BAEKELAND, Sc.D.

WHILE I appreciate deeply the distinction of speaking before you on the occasion of the Fiftieth Anniversary of the Columbia School of Mines, I realise, at the same time, that nobody here present could do better justice to the subject which has been chosen for this lecture than the beloved master in whose honour the Charles Frederick Chandler Lectureship has been created.

Dr. Chandler, in his long and eminently useful career as a professor and as a public servant, has assisted at the very beginning of some of the most interesting chapters of applied chemistry, here and abroad.

Some of his pupils have become leaders in chemical industry; others have found in his teachings the very conception of new chemical processes which made their names known throughout the whole world.

Industrial chemistry has been defined as "the chemistry of dollars and cents."

This rather cynical definition, in its narrower interpretation, seems to ignore entirely the far-reaching economic and civilising influences which have been brought to life through the applications of science; it fails to do justice to the fact that the whole fabric of modern civilisation becomes each day more and ever more interwoven with the endless ramifications of applied chemistry.

The earlier effects of this influence do not date back much beyond one hundred and odd years. They became distinctly evident during the first French Republic, increased under Napoleon, gradually spread to neighbouring countries, and then reaching out farther, their influence is now obvious throughout the whole world.

France, during the revolution, scattered to the winds old traditions and conventionalities, in culture as well as in politics. Until then, she had mainly impressed the world by the barbaric, wasteful splendour of her opulent kings, at whose courts the devotees of science received scant attention in comparison to the more ornamental artists and belles-lettres, who were petted and rewarded alongside of the all-important men of the sword.

In fact, as far as the culture of science was concerned, the Netherlands, Germany, and Italy, and more particularly England, were head and shoulders above the France of "le Roi Soleil."

The struggles of the new régime put France in the awkward position of the legendary beaver which "had to climb a tree."

If for no other reason, she needed scientists to help her in her wars against the rulers of other European nations. She needed them just as much for repairing her crippled finances and her badly disturbed industries which were dependent upon natural products imported until then, but of which the supply had suddenly been cut off by the so-called Continental blockade. Money prizes and other inducements had been offered for stimulating the development of chemical processes, and—what is more significant—patent laws were promulgated so as to foster invention.

Nicolas Leblanc's method for the manufacture of soda to replace the imported alkalis, Berthollet's method for bleaching with chlorine, the beet-sugar industry to replace cane-sugar imported from the colonies, and several other processes, were proposed.

All these chemical processes found themselves soon lifted from the hands of the secretive alchemist or the timid pharmacist to the rank of real manufacturing methods: Industrial chemistry had begun its lustrous career.

First successes stimulated new endeavours and small wonder is it that France, with these favourable conditions at hand, for a while at least, entered into the most glorious period of that part of her history which relates to the development of chemistry and the arts dependent thereon.

It is difficult to imagine that, at that time, Germany, which now occupies such an enviable position in chemistry, was so far behind that even in 1822, when Liebig wanted to study chemistry at the best schools, he had to leave his own country and turn to Gay-Lussac, Thénard, and Dulong in Paris.

But the British were not slow to avail themselves of the new opportunities in chemical manufacturing so clearly indicated by the first successes of the French. Their linen bleacheries in Scotland and England soon used an improved method for bleaching with chloride of lime, developed by Tennant, which brought along the manufacture of other chemicals relating thereto, like sulphuric acid and soda.

The chemical reactions involved in all these processes are relatively simple, and after they were once well understood, it required mainly resourceful engineering and good commercial abilities to build up successfully the industries based thereon.

From this epoch on dates the beginning of the develop-

\* The Chandler Lecture, Columbia, U S A, 1914.



ment of that important industry of heavy chemicals in which the British led the world for almost a century.

In the same way, England had become the leader in another important branch of chemical industry—the manufacture of coal-gas.

The Germans were soon to make up for lost time. Those same German universities, which when Liebig was a young man were so poorly equipped for the study of chemistry, were now enthusiastically at work on research along the newer developments of the physical sciences, and, before long, the former pupils of France, in their turn, became teachers of the world.

Liebig had inaugurated for the chemical students working under him his system of research laboratories; however modest these laboratories may have been at that time, they carried bodily the study of chemistry from pedagogic boredom into a captivating cross-examination of nature.

And it seemed as if nature had been waiting impatiently to impart some of her secrets to the children of men, who for so many generations had tried to settle Truth and Knowledge by words and oratory and by brilliant displays of metaphysical controversies.

Indeed, at that time, a few kitchen tables, some clumsy glassware, a charcoal furnace or two, some pots and pans, and a modest balance were all that was needed to make nature give her answers.

These modest paraphernalia, eloquent by their very simplicity, brought forth rapidly succeeding discoveries. One of them was truly sensational: Liebig and Wohler succeeded in accomplishing the direct synthesis of urea; thinking men began to realise the far-reaching import of this revolutionary discovery whereby a purely organic substance had been created in the laboratory by starting exclusively from inorganic materials. This result upset all respected doctrines that organic substances are of a special enigmatic constitution, altogether different from inorganic or mineral compounds, and that they only could be built up by the agency of the so-called "vital force"—whatever that might mean.

Research in organic chemistry became more and more fascinating; all available organic substances were being investigated one after another by restless experimentalists.

Coal-tar, heretofore a troublesome by-product of gas manufacture, notwithstanding its uninviting, ill-smelling, black, sticky appearance, did not escape the general inquisitive tendency; some of its constituents, like benzol or others, were isolated and studied.

Under the brilliant leadership of Kékulé, a successful attempt was made to correlate the rapidly increasing new experimental observations in organic chemistry into a new theory which would try to explain all the numerous facts; a theory which became the sign-post to the roads of further achievements.

The discovery of quickly succeeding processes for making from coal-tar derivatives numerous artificial dyes, rivalling, if not surpassing, the most brilliant colours of nature, made the group of bold investigators still bolder. Research in organic chemistry began to find rapid rewards; entirely new and successful industries based on purely scientific data were springing up in England and France, as well as in Germany.

Some wideawake leaders of these new enterprises, more particularly in Germany, soon learned that they were never hampered by too much knowledge, but that, on the contrary, they were almost continuously handicapped in their impatient onward march by insufficient knowledge, or by misleading conceptions, if not by incorrect published facts.

This is precisely where the study of organic chemistry received its greatest stimulating influence and soon put Germany, in this branch of science, ahead of all other nations.

Money and effort had to be spent freely for further research. The best scholars in chemistry were called into action. Some men, who were preparing themselves to

become professors, were induced to take a leading part as directors in one or another of the new chemical enterprises. Others, who refused to forsake their teachers' career, were retained as advisers or guides, and, in several instances, the honour of being the discoverers of new processes, or a new dye, was made more substantial by financial rewards. The modest German university professor, who heretofore had lived within a narrow academic sphere, went through a process of evolution, where the rapidly growing chemical industry made him realise his latent powers and greater importance, and broadened his influence way beyond the confines of his lecture-room. Even if he were altruistic enough to remain indifferent to fame or money, he felt stimulated by the very thought that he was helping, in a direct manner, to build up the nation and the world through the immediate application of the principles of science.

In the beginning, science did all the giving and chemical industry got most of the rewards; but soon the rôles began to change to the point where frequently they became entirely inverted. The universities did not furnish knowledge fast enough to keep pace with the requirements of the rapidly developing new industries. Modern research laboratories were organised by some large chemical factories on a scale never conceived before, with a lavishness which made the best equipped university laboratory appear like a timid attempt. Germany, so long behind France and England, had become the recognised leader in organic manufacturing processes, and developed a new industrial chemistry based more on the thorough knowledge of organic chemistry than on engineering skill.

In this relation, it is worth while to point out that the early organic industrial chemistry, through which Germany was soon to become so important, at first counted its output not in tons, but in pounds—not in size nor in quantity, but in variety and quality.

(To be continued).

## ON THE ACTION OF LEAD, COPPER, TIN, NICKEL, ZINC, AND ALUMINIUM ON WATER.

By Dr. W. P. JORISSEN, The University, Leiden, Holland.

(Continued from p. 58).

### 4. Dissolved Substances in Water.

If we wish to study the processes which take place with the corrosion of metals in contact with air and water as found in nature, we have of course to take into account the dissolved substances.

Now, as a rule, we have to deal with several kinds of water—rain-water, surface water, subsoil water, deep-well water, spring water, river water, sea-water.

Rain-water often does not differ much from distilled water. Again, it often contains a considerable quantity of salts, &c.; for instance, in the neighbourhood of the sea and in manufacturing towns. Extensive communications about the amount of nitrogen as ammonia and nitric acid and of chlorides in the rain-water have been made by N. H. J. Miller (Note 16). In the neighbourhood of the German Ocean (Helder, Holland) I found an average Cl concentration of 32.5 mgrms. per litre (Note 17)—a much higher figure than those mentioned by Miller. S. Wolff (Note 18) often observed at Newton Heath, near Manchester, a considerable hardness, probably caused by flue dust.

It is a well-known fact that the other kinds of water, with the exception of sea-water, contain a number of substances in varying quantities and of different kinds. Sea-water, however, if not in abnormal conditions, contains a mixture of salts of constant composition (Note 19), which is often given as follows (Note 20):—

Solution.	Iron.	Zinc.	Copper.	Aluminium.
Chromic acid . . . .	Inhibits.	0.1 per cent inhibits; 1 per cent acts on the metal.	Inhibits.	Inhibits.
Potassium dichromate .	Inhibits.	Inhibits.	Inhibits.	Inhibits.
Potassium chromate . .	Inhibits.	Inhibits.	Inhibits.	Inhibits.
Sodium carbonate . . .	Inhibits.	2 per cent inhibits; 1 per cent allows some action.	5 per cent inhibits; stronger solutions act on the metal.	Acts on the metal with evolution of hydrogen.
Borax . . . . .	Inhibits.	1 per cent inhibits.	Inhibits.	Retards.
Potassium hydroxide . .	Inhibits.	1 per cent inhibits; stronger solutions have a direct action.	Allows.	Acts on the metal with evolution of hydrogen.
Potassium iodide . . .	Allows.	Allows.	--	Allows.
Potassium iodate . . .	Inhibits.	Allows.	Acts on the metal producing blackening.	Inhibits.
Potassium bromate . . .	Inhibits (after slight initial action).	Allows (acts on the metal.	--	--
Potassium ferrocyanide	Inhibits.	Inhibits.	Produces film on the metal.	Inhibits.
Potassium ferricyanide .	Allows.	Allows.	Produces film on the metal.	Allows.

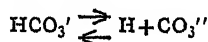
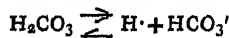
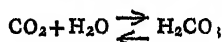
	Per cent.
NaCl . . . . .	77.758
MgCl <sub>2</sub> . . . . .	10.878
MgSO <sub>4</sub> . . . . .	4.737
CaSO <sub>4</sub> . . . . .	3.600
K <sub>2</sub> SO <sub>4</sub> . . . . .	2.465
MgBr <sub>2</sub> . . . . .	0.217
CaCO <sub>3</sub> . . . . .	0.345

It need hardly be said that it is preferable to represent the analytical results as follows (Note 21):—

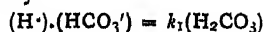
	Per cent.
Na <sup>+</sup> . . . . .	30.61
Mg <sup>++</sup> . . . . .	3.83
Ca <sup>++</sup> . . . . .	1.20
K <sup>+</sup> . . . . .	1.11
Cl <sup>-</sup> . . . . .	55.18
SO <sub>4</sub> <sup>==</sup> . . . . .	7.67
HCO <sub>3</sub> <sup>'</sup> (and CO <sub>3</sub> <sup>''</sup> ) . . .	0.21
Br <sup>-</sup> . . . . .	0.19

As not only the above salts, but all those which may be formed by the ions, mentioned in the second table, will be present. Of course, it is impossible to say anything definite about the concentration of the non-ionised molecules of these salts in so complicated a solution as sea-water.

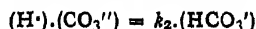
As regards carbonic acid and carbonates in water the following remarks may be made:—If only free carbonic acid is present, we have the equilibria—



and consequently—



and—



or—

$$\frac{(\text{HCO}_3')}{(\text{H}_2\text{CO}_3).(\text{CO}_3'')} = \frac{k_1}{k_2}$$

in which the symbols (H<sup>+</sup>), &c., denote the concentration of the ions H<sup>+</sup>, &c., in grm. molecules per litre, and  $k_1$  and  $k_2$  the first and second dissociation constants of carbonic acids about  $3 \cdot 10^{-7}$  (Note 22) and  $6 \cdot 10^{-11}$  respectively (Note 23).

If carbonates and hydrocarbonates are also present, analogous equilibria exist, and we again have the equation—

$$\frac{(\text{HCO}_3'')}{(\text{H}_2\text{CO}_3).(\text{CO}_3'')} = \frac{k_1}{k_2} = 5000$$

or—

$$(\text{CO}_3'') = \frac{(\text{HCO}_3'')}{5000(\text{H}_2\text{CO}_3)}$$

If the quantity of carbonates will be exceedingly small if free carbonic acid is present.

This equation will be used in this report especially in the case of the corrosion of lead.

There, as in other cases, I shall have occasion to refer to the specific influence of a number of other substances or their ions on the corrosion of metals. Here attention will only be drawn to the fact that those ions which show no specific action may yet accelerate corrosion processes if attributable to "galvanic actions." For they increase the conductivity of the water, and in this way the strength of the electric current.

##### 5. Passivity of Metals.

\* Yet another phenomenon caused by a number of substances and annihilated by others claim our attention, viz., the passivity shown by several metals under certain circumstances.

First of all from a paper by W. R. Dunstan and J. R. Hill on the aerial oxidation of metals (Note 24) a table summarising the results of their experiments on the effect of various solutions on the oxidation of iron, zinc, copper, and aluminium is here reproduced. (Magnesium has been omitted by me).

Now, all the substances mentioned in this table which inhibit the rusting of iron also render it passive (Note 25).

Before speaking about the other metals in this table, it is perhaps better to tell how the passivity is tested.

As testing liquids Dunstan and Hill make use of distilled water (observing whether rusting occurs), a solution of nitric acid of specific gravity (1.2) or a dilute solution of copper sulphate (0.5 per cent). In applying these tests some precautions have to be made. A hole is previously bored in the sheet of metal; a very thin glass rod, bent into a hook at one end, is inserted in the hole. In this way it is possible to lift the metal sheet from the solution which has made it passive or not (after, say, twelve hours' immersion), wash it with distilled water without touching it with the hands or shaking it too violently, and immerse it in the testing liquid, whereupon the rod is removed. Or a simpler method may be used, which consists in pouring off the solution, rinsing out the vessel several times with distilled water, quickly pouring the testing liquid over the metal so as to completely cover it. All this should be done as rapidly as possible, without unduly shaking the metal.

Dunstan and Hill (Note 26) found that zinc is rendered passive by a 1 per cent solution of potassium dichromate, by solutions of chromic acid between 0.01 and 0.1 per cent, by a 1 per cent solution of potassium chromate, but not so completely as is done by potassium dichromate. Two per cent solutions of sodium carbonate and of borax also render zinc partly passive. Copper is rendered passive by solutions of chromic acid, potassium dichromate, and chromate. About a possible passivity of aluminium nothing is said by Dunstan and Hill. They incidentally mention that lead appears to behave similarly to copper and zinc.

From their experiments the conclusion may be drawn that the agents which prevent rusting render the metal passive.

This report is not the place to discuss the theories (Note 27) which have been put forward to explain the passive state of metals (especially of iron); Dunstan and Hill conclude that it is due to the presence of a film of oxide, which is also the opinion of several other investigators (Note 28).

It only remains to tell how passivity is destroyed. With iron this has been studied extensively. Touching with the fingers, violently shaking against the sides of the vessel, scratching of the surface, touching with zinc or active iron when immersed in copper sulphate solution or in nitric acid (sp. gr. 1.2) destroy its passive state. The same result is brought about by dilute sulphuric acid, hydrochloric acid, acetic acid, carbonic acid, solutions of sodium chloride, &c.

Passive zinc is vivified by scratching. Salt solutions and carbonic acid do not act so readily. Zinc loses largely its passivity on washing with alcohol and drying. Dilute sulphuric acid, hydrochloric acid, a solution of ferrous sulphate, for instance, destroy the passivity of copper; washing in alcohol has the same effect.

A special kind of passivity still claims our attention, viz., that caused by absolute purity.

B. Lambert and J. C. Thomson (Note 29), who have prepared the purest iron which has been made until now by taking every precaution against contamination, observed that this metal was not corroded by pure air (totally free from carbonic acid) and pure water even in the course of two years (Note 30). Under quite the same circumstances Lambert (Note 31) observed corrosion when using strips of commercial pure electrolytic iron, pure iron of Kahlbauer, or a cylinder made from a soft iron nail. All three had been polished by fine carborundum powder and Swedish filter paper.

When the pure iron prepared by Lambert and Thomson was partly pressed by an agate in an agate mortar, it soon corroded on the pressed places. The metal when thus treated seems to lose its complete uniformity of surface.

## 6. Influence of Stress.

That a different treatment of different parts of a metal object may cause an acceleration of corrosion is well known. As regards the galvanic activity exhibited between strained and unstrained pieces of the same iron, the observations of Andrews, Hambuchen, Richard, and Behr, and Heyn and Bauer (Note 32) may be mentioned. In most cases the strained iron has been found to be more liable to corrode. The difference of potential between the strained and unstrained piece is very small, however, and local circumstances appear to be apt to reverse the direction of the current. W. Spring (Note 33) took two wires of the same metal (tin, lead, bismuth), and heated one of them to a temperature below but near its melting point. The heated wires thus lost their strain and returned to their normal condition. By immersing the strained wire and the normal one in a solution of one of the salts of the metal, he found a small difference of potential which did not exist beforehand. In the case of tin and lead wires (placed in stannous chloride and lead nitrate solutions respectively) the strained wires were found to be the dissolving electrodes (anodes); bismuth, however, showed an opposite tendency.

Now, Ernst Cohen (Note 34) has studied some interesting cases of nucleus action on grain growth in metals. Thus tin, when dulled in some way, will inoculate bright cold-worked tin with similar dullness.

In the case of cold-rolled lead, where grain growth has been first observed by J. A. Ewing and W. Rosenhain, the process is, according to H. Baucke's experiments (Note 35), accelerated considerably by dilute acetic acid, a galvanic cell Pb (strained)-electrolyte-Pb (normal) being obtained. Now this cold-rolled lead, and also lead tubes, often show corrosion when in contact with electrolytes, of which Baucke mentions a few cases. Micrographic observation showed that grain growth had taken place. The corrosion had penetrated between the large crystals.

Observations about the internal stresses of cold-worked metals have been made by E. Heyn and O. Bauer (Note 36). With a cold-rolled rod, for instance, the outer layer is in a state of tension, while the inner core is in a state of compression. In consequence of these stresses cracking of aluminium vessels through corrosion has been observed (Note 37).

## 7. Influence of Surface.

The few remarks made above will have fixed the attention on the influence of the surface of a metal on its corrosion.

The possible influence of fine or coarse crystallisation, polish, unevenness of surface, porosity, laminations, impurities, adsorption and occlusion of gases and liquids, &c., may be mentioned.

That an increase of surface had an accelerating influence is a well-known fact.

Again, an excessive pulverisation of the metal may change the aspect of the corrosion process. Thus, iron powder liberates hydrogen from water even at ordinary temperatures (Note 38). To what extent impurities play a part in this process has not been definitely settled. Iron oxide, formed beforehand by exposing the iron powder to the air, seems to accelerate the reaction (Note 39).

## 8. Galvanic Action.

About the galvanic action exhibited between a metal and its impurities something has already been remarked with regard to zinc. With iron many observations have been made (Note 40). Irregularity of composition or heterogeneity and surface impurities may easily give rise to galvanic actions. The local actions which take place appear in patches of rust and pitting.

That galvanic action may be observed between pieces of different kinds of iron when immersed in water need hardly be mentioned (Note 41), still less that it occurs between pieces of different metals (Note 42).

About the change which the E.M.F. undergoes here in

the course of time very little is known. About the chemical processes which take place hardly anything has been published. My own experiments in this direction are not in a sufficiently advanced state to be described here.

It is evident that having to deal with the galvanic action between different metals the series of electrochemical potentials is not the only thing to be consulted, but the overvoltage has equally to be taken into account. For instance, it would be deducted from the said series that tin is worse than iron for accelerating the corrosion of zinc; the correction for overvoltage shows, however, that it is far less harmful.

Everybody knows that the corrosion of a metal when immersed in an electrolyte can be lessened or prevented by connecting it with another metal higher in the above series, and may be accelerated by connecting it with a lower-placed one. In practice many cases are met with (Note 43). Of course it is also possible to accelerate or prevent the corrosion by making the metal respectively the anode or cathode of an electrolytic cell. This direct use of electric currents has been the basis of a number of patents for the protection of boilers and condensers, for it is more economical and seems to be more effective than the connection with a "more electro-positive" metal (Note 44).

After the above general remarks the six metals named in the heading of this report will be treated separately.

#### Notes.

16. *Journ. Agricultural Science*, 1905, i., 280.
17. W. P. Jorissen, *Chem. Weekbl.*, 1906, iii., 647.
18. *Journ. Soc. Chem. Ind.*, April 15, 1913.
19. Compare E. Ruppin, "Publ. de Circonstance" No. 55, 1910.
20. Dittmar, "Reports Scientific Results Expl. Voyage H.M.S. *Challenger*—Physics and Chemistry," 1884, i.
21. Compare W. P. Jorissen, "Phys. Chem. Investigations of Sea-water," *Chem. Weekbl.*, 1904, i., 730.
22. J. Walker, *Journ. Chem. Soc.*, 1900, lxxvii., 5; G. Bodländer, *Zeit. Phys. Chem.*, 1900, xxxv., 23.
23. Auerbach and Pick, *Arch. Kais. Gesundh. amt.*, 1911, xxxviii., 243.
24. *Journ. Chem. Soc.*, 1911, xcix., 1835.
25. Several other substances, not mentioned here, also render iron passive.
26. The passivity of iron and other metals, *Journ. Chem. Soc.*, 1911, xcix., 1853.
27. *Jahrb. d. Radioakt. u. Elektronik*, 1911, viii.
28. See, however, e.g., E. Grave, *Zeit. Phys. Chem.*, 1911, lxxvii., 513.
29. *Journ. Chem. Soc.*, 1910, xcvi., 2430.
30. Lambert, *Ibid.*, 1912, ci., 2068.
31. *Ibid.*, 1912, ci., 2056.
32. All described in Newton Friend's "The Corrosion of Iron and Steel," 1911, 242-247.
33. *Bull. Acad. Roy. d. Belg.*, 1903, No. 12, 1033.
34. *Zeit. Phys. Chem.*, 1909, lxxvii., 214.
35. *Internat. Zeit. f. Metallurg.*, 1912, ii., 243.
36. *Ibid.*, 1911, i., 16.
37. Compare Heyn and Bauer, *Mitt. Konigl. Materialpruf.-amt Gros-Lichterfelde West*, 1911, xxix., 2.
38. Compare S. Birnie, *Chem. Weekbl.*, 1907, iv., 291, and the literature cited by him; also W. van Rijn, *Ibid.*, 1908, v., 1.
39. Guibourt, cited by Ramann, *Ber.*, 1881, xiv.
40. See, for instance, those mentioned by Newton Friend, *loc. cit.*, 247-254.
41. *Ibid.*, 254-262.
42. e.g., W. P. Jorissen, *Jaarversl. Techn. Geselsch.*, Delft, 1911-12 (1913); about the galvanic action between iron and other metals, see also Newton Friend, *loc. cit.*, 262-268.
43. Vide W. P. Jorissen, *loc. cit.*
44. Compare W. W. Haldane Gee, *Journ. Soc. Chem. Ind.*, May 31, 1913.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, January 21, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Atmospheric Electricity Potential Gradient at Kew Observatory, 1898-1912." By Dr. C. CHREE, F.R.S.

A previous paper discussed results obtained from the Kelvin water-dropping electrophograph at Kew Observatory for the period 1898 to 1904. The present paper discusses the data from the fifteen years 1898 to 1912.

In 1909 a number of experiments were made which led to improvements in the apparatus for determining absolute values of potential gradient and in the methods employed. This has led to a reconsideration of the absolute values obtained with the old apparatus in earlier years.

Particular attention is given to the character of the diurnal variation, as to how it varies throughout the year, and as to the nature of the differences apparent between different years. The predominance of the 12-hour term over the 24-hour term in the diurnal variation, which is especially conspicuous in summer, is found to vary greatly from year to year. The 12-hour term shows less fluctuations either in amplitude or phase than the 24-hour term.

A comparison is made between the results obtained at Kew in 1912 and those obtained during the same year at Edinburgh by Messrs. Carse and Shearer.

"The Transmission of Electric Waves over the Surface of the Earth." By Prof. A. E. H. LOVE, F.R.S.

An analytical solution of the general equations of electrodynamics is obtained for the case of waves generated by a vibrating doublet in presence of a conducting sphere, and is adapted to obtain the known solution for perfect conduction, and the correction for moderate resistance, such as that of sea-water. The known solution is expressed by the sum of a series involving zonal harmonics, and the correction by a similar series. Different results have been obtained by different writers who have investigated the numerical value of the former sum. In the paper a new method of summing the series is explained and worked out in detail for the wave-length 5 km. In the case of perfect conduction the result confirms that found by H. M. Macdonald, *Proc. Roy. Soc., A*, 1914, xc., 50. The effect of resistance is found to be a slight increase of the strength of the signals at considerable distances, counteracting to some small extent the enfeebling effect of the curvature of the surface. A comparison is instituted between the results of the theory and those of recorded experiments. From these it had previously been inferred that the diffraction theory fails to account for the facts; but, after a discussion of the experimental evidence, it appears that the observations may admit of a different interpretation, according to which the results of the diffraction theory would be in good agreement with those of daylight observations at great distances.

"Electromagnetic Waves in a Perfectly Conducting Tube." By L. SILBERSTEIN.

The problem of waves in conducting tubes, which has already been treated by various authors, is here taken up with the purpose of developing some of its solutions which offer noteworthy peculiarities with respect to the velocity of the corresponding waves. The waves investigated are axially symmetrical and of permanent type. Their velocity of transfer along the tube is a comparatively simple function of the period of vibration and of the "order" of waves, and it exceeds, for each of these waves, the velocity of light in free space. The peculiarities of distribution of the lines of force are illustrated by two examples with annexed drawings. The paper closes with remarks con-

cerning superpositions of waves of the specified kind, more especially of electromagnetic pulses.

"An Electrically Heated Full Radiator." By H. B. KEENE.

The essential conditions in a determination of the constant of the Stefan-Boltzmann law of radiation are, either that both "emitter" and "receiver" are full radiators, or that the amount by which they fall short of full radiators is known—an amount difficult to determine with certainty. Hitherto, a measurement of this constant has not been made under full radiation conditions.

This paper describes an electrically heated "constant temperature enclosure" which has been constructed for temperatures in the neighbourhood of  $1700^{\circ}\text{C}$ . It consists of a hollow cylinder of alumina, about 8 inches in diameter, closed with conical end pieces of the same material. Three separate windings of platinum strip provide a means of adjusting the temperature distribution within the enclosure, which can be made uniform to within two or three degrees. At the apex of one of the cones is a circular aperture which emits radiation closely approximating to full radiation.

It is intended to use this radiator in conjunction with a full receiver, described in an earlier paper, in order to determine the value of the radiation constant under "black body" conditions.

## NOTICES OF BOOKS.

*The Spectroscopy of the Extreme Ultra-violet.* By THEODORE LYMAN, Ph.D., Assistant Professor of Physics at Harvard University. London: Longmans, Green, and Co.

ALTHOUGH the title of the above work refers to the extreme ultra-violet, in point of fact the author deals with the spectrum from the most refrangible recorded radiation down to the visible violet at  $\lambda 4000$ .

Spectroscopy in itself is naturally a fascinating science, and the interest deepens as we approach the limit that can be recorded upon the photographic plate. In this region photoelectric, photochemical, bactericidal, and ionisation effects are at a maximum; but perhaps the greatest interest in the rays of short wave-length is through their bearing upon the recent discovery that X-rays are due to radiations of the same character differing only in their extreme shortness of about one Angstrom unit. Between this value and that of the shortest recorded luminous radiation of 905 Angstrom unit lies a gap of unexplored ground that may be responsible for "many things."

The exploration of this region is at the present moment proceeding in both directions, from the X-rays towards radiations of greater wave-length, and from the ultra-violet or Schumann rays.

The book is an account of research in this latter direction undertaken at the Harvard University.

The author has not only given a concise review of the literature of the subject, but he has also recorded with it a large amount of valuable data and technical detail that has been obtained in the research.

Part I. contains only two chapters; the first is devoted to photometry and the three chief methods for estimating the intensity of radiation, the photographic plate, the photoelectric cell, and the bolometer and radiometer. The second chapter deals with the absorption of solids and gases for the ultra-violet, and a deal of very useful information is given. Fused quartz has been found to be less transparent than plates of the crystalline variety when cut perpendicular to the axis; the absorption by air begins to show itself in the region on the more refrangible side of  $\lambda 2000$ ; the active agent is probably oxygen. Part I. concludes with a short discussion on the reflecting power of metals.

Part II., which is the main portion of the book, opens a biography of the late Victor Schumann, whose extraordinary mechanical ability enabled him to construct apparatus by which he succeeded in extending our knowledge of the hydrogen spectrum to about  $\lambda 2000$ ; full details are then given of the construction of vacuum spectroscopes at Harvard and of experiments carried out with them; this practically occupies the remainder of the book, and includes the Absorption of Solids, Emission Spectra of Gases, Emission Spectra of Solids, and concludes with a discussion upon the limit of the spectrum. At the end of the book extensive tables are given of the wave-lengths of lines in the spectra of hydrogen, nitrogen, argon, carbon monoxide, &c., and many of the metallic elements. The book ends with a valuable bibliography of citations that occur in the text and a short appendix giving notes of photographic emulsions and developers.

*The Chemistry of Cyanogen Compounds.* By HERBERT E. WILLIAMS. London: J. and A. Churchill. 1915.

ALTHOUGH the technology of the derivatives of cyanogen has been made the subject of several text-books in recent years, the chemistry of these compounds has not been exhaustively discussed in any treatise, and this volume, in which special attention is paid to the purely scientific aspects of their production and properties, will be welcomed by those interested in the use of them. The abundant literature of the subject has been carefully searched, and some of the results of the author's own work, not hitherto published, are described. A short account is also given of the manufacture, application, and estimation of the compounds. As a compilation the book appears satisfactory, and the author may be congratulated upon having successfully performed a tedious and somewhat difficult task.

*The British Journal Photographic Almanac, 1915.* Fifty-fourth issue). Edited by GEORGE E. BROWN, F.I.C. 1068 pages, Crown 8vo. London: Henry Greenwood and Co., Ltd.

THE "British Journal Photographic Almanac" is an annual publication which by its very size and price attracts the purchaser. The fifty-fourth annual volume, just issued, for 1915 contains the customary guide to the photographic processes from the making of the negative to the printing or enlargement by the many methods now available to the amateur. The editor's article deals fully with the making of enlargements, whilst Dr. Duncan J. Reid writes most explicitly on "Photography under the Microscope." Both subjects are fully illustrated. The descriptions of new introductions in cameras, lenses, &c., are a further useful section, whilst under the heading "Epitome of Progress" over 100 pages are devoted to recording the hints, formulæ, and methods advocated by practical workers during the past twelve months. Separate indexes—to the text and to the endless goods advertised—are provided, and efficiently refer the reader to the place of every item of information in the bulky volume.

*Intermediate Practical Chemistry.* By FREDERICK WILLIAM ATTACK, M.Sc.Tech. (Manchester), B.Sc. (London). London: Sherratt and Hughes.

STUDENTS who intend to proceed to an Honours degree will find this book a useful laboratory guide. Some elementary work, including easy preparations of the non-metals and their compounds, is first described, and the usual qualitative analytical processes follow; while this section exhibits no special novelty, the tables in it are very clear and the directions concise. Methods of investigating the sensitiveness of different tests are added, and the identification of compounds of the rarer elements is included. In a chapter on quantitative analysis the general principles of volumetric work are described, and the details of some straightforward applications of them are given.



*The Farmer as a Manufacturer.* By A. T. STUART, B.A. Dominion of Canada: Department of Agriculture, Experimental Farms.

THIS pamphlet contains an outline of the principles of agricultural chemistry expressed in very simple and non-technical language, so that they can easily be grasped by the unscientific reader. It is graphically written, and the author shows considerable skill in putting the information into the form which is most likely to make an impression upon the practical man's mind. The requirements of man in the way of food and clothing are first discussed, and the work of plants in providing materials to supply these wants is sketched. The chemistry and physics of different kinds of soils and methods of maintaining their fertility are then considered, and finally the compositions of important feeding stuffs and foods are tabulated. The farmer will be able to get by the study of the pamphlet a clear idea of the way in which he should use the natural raw materials to obtain the best and most profitable yield of protein, fats, and carbohydrates.

*Report of the Dominion Chemistry, Experimental Farms, Department of Agriculture.* Ottawa: Government Printing Bureau. 1914.

THIS report describes the chemical research work of the staff of the Dominion Experimental Farms during the year ending March, 1913, and also gives the results of the routine work which has been done for the assistance of farmers who have submitted samples for analysis. The information and advice given to the practical man are much appreciated, and the amount of work done is steadily increasing year by year. The tables of results of analyses and the comments and hints based upon them will be of use to farmers in other countries than Canada. The research work done during the year included the continuation of the investigations of the conservation of soil moisture, the influence of environment on the composition of wheat, and the cultivation of the sugar-beet for factory purposes.

*Australia's Trade with Germany.* Published under the Authority of the High Commissioner for the Commonwealth of Australia, 72, Victoria Street, London.

THIS pamphlet contains a reprint of the High Commissioner's letter to the *Times* on the subject of Australia's trade with Germany, and an article in which special emphasis is laid upon the sale of copper and lead and concentrates to Germany. Summaries are given of exports and imports between the two countries, as well as detailed tables, and also very full lists of the exporters of Australia's principal products. Further information may be obtained from the High Commissioner, and information relating to the individual States from the various Agents-General in London. A study of the pamphlet will speedily convince the British merchant that there can never be a better chance than at present of capturing German trade by capturing Australia's raw materials.

*The Constitution of the Natural Silicates.* By FRANK WIGGLESWORTH CLARKE. Washington: Government Printing Office. 1914.

IN this bulletin the author describes in detail the work which has been done on the elucidation of the problem of the nature and structure of the natural silicates. The determination of their empirical formulae is first described, followed by the investigation of their physical properties and the natural alterations they undergo. The results which have been obtained in the artificial synthesis of the silicates are then described, and from all the data thus accumulated the constitutional formulae are finally deduced. Only brief allusion is made to the hexite pentite theory, but the monograph is, on the whole, complete in detail, and the subject is treated systematically and with great lucidity.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clix., No. 24, December 14, 1914, No. 25, December 21, 1914.

These numbers contain no chemical matter.

No. 26, December 28, 1914.

**Influence of Gaseous Impurities in Silver upon the Values of Atomic Weights Determined by Classical Methods.**—Ph. A. Guye and F. E. E. Germann.—The authors' researches show that owing to the gases retained by silver the value given by classical methods for the atomic weight of chlorine must be corrected, being replaced by a rather higher number. The atomic weight of silver itself, and those of metals or metalloids determined by the ratio to a halogen salt, must also be modified.

**Determination of Iodine Indices in Alcoholic Liquids.**—R. Marcille.—When iodine indices are determined in alcoholic liquids by Hübl's method the volume of solution employed must be the same, and at the same temperature in all the experiments; for example, 100 cc. at 50°. The chloro-iodomercuric solution (30 cc.) must be added in a dark room, and the flasks must be kept in the dark during the contact.

## MISCELLANEOUS.

**The Biochemical Society.**—It has been decided to postpone the Meeting of the Society arranged to be held in Leeds on February 13, 1915, until circumstances are more favourable. The next meeting will be the Annual General Meeting, at St. Bartholomew's Hospital, on Thursday, March 11, 1915.

**Royal Institution.**—A General Meeting of the Members of the Royal Institution was held on the 1st inst., the Duke of Northumberland, K.G., President, in the chair. The special thanks of the members were returned to Dr. H. D. Rolleston for his generous gift, in the name of Miss Davy (niece of Sir Humphry Davy), of a bust of Sir Humphry Davy, executed in 1822 by Samuel Joseph. The bust was presented to the Institution on behalf of Dr. Rolleston by Prof. Sir James Dewar, after his Friday evening discourse on January 22, and accepted by the Treasurer on behalf of the members.

## MEETINGS FOR THE WEEK.

- TUESDAY, 9th.—Royal Institution, 3. "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S.  
 WEDNESDAY, 10th.—Royal Society of Arts, 8. "British Lithography in 1911," by E. Vincent Brooks.  
 THURSDAY, 11th.—Royal Institution, 3. "Zoological Studies: War and Evolution, Nations as Species," by P. Chalmers Mitchell, F.R.S.  
 — Royal Society of Arts, 4.30. "Tribes of the Brahmaputra Valley," by Capt. Sir George Dull Dunbar, Bart.  
 — Royal Society. "*Lepidostrobis kentuckiana*," formerly "*Lepidostrobis fischeri*" (Scott and Jellrey)" (a Correction), by D. H. Scott. "The Excretory Process in the Dog's Heart. Part II, The Ventricle," by T. Lewis and M. A. Rothchild. "Variation in the Growth of Mammalian Tissue *in vitro* according to the Age of the Animal," by A. J. Walton.  
 FRIDAY, 12th.—Royal Institution, 9. "Recent Advances in Oceanography," by William S. Bruce, F.R.S.E.  
 — Alchemical, 8.15. "Alchemy and the Devil," by The Ven. Archdeacon Craven, D.D.  
 — Physical, 8. "Criterion of Steel Suitable for Permanent Magnets," by S. P. Thompson. "Galvanic Cell which Reverses its Polarity when Illuminated," by A. A. C. Swinton. "Investigation on the Photographic Effect of Recoil Atoms," by A. B. Wood and A. J. Steven.  
 SATURDAY, 13th.—Royal Institution, 3. "Emergency Music," by H. Walford Davies, Mus.Doc. (Illustrated by a small Choir).

# THE CHEMICAL NEWS.

VOL. CXI., No. 2882.

## THE COMMERCIAL CLASSIFICATION OF REFINED COPPER.\*

By LAWRENCE ADDICKS.

ANY adequate classification of a material of commerce such as copper must take into account both the limitations of the metallurgical processes by which the material has been obtained and the needs of the manufacturing processes in which it is to be employed. The metallurgical methods depend in turn upon the nature of the ores or other sources of supply, and the manufacturing ones upon the ultimate uses of the finished product.

The world's copper supply comes from four main sources, sulphide ores, oxidised ores, native ores, and scrap. Perhaps the chief chemical characteristic of copper is its affinity for sulphur, and the largest deposits of copper ores consist of more or less complex sulphides. Near the surface these ores are frequently altered to oxides and carbonates by atmospheric influence, and there are also large deposits entirely free from sulphur. Native copper ores where the copper exists as free metal occur in various parts of the world in small quantities, but notably in the enormous deposits in the northern peninsula of Michigan, where they form the source of the so-called Lake Copper.

Metallurgically there are three typical processes for producing crude or unrefined copper from the ore, based on the general principles of oxidising sulphides and reducing oxides, (a) roasting, smelting, and converting, (b) alternate oxidation and reduction, and (c) direct reduction of oxidised ores. (a), which is a strongly oxidising process by which the great majority of the American production is made from sulphide ores, results in the almost complete elimination of impurities which have volatile oxides, including some of the worst enemies of refined copper, such as arsenic. Converter bar nearly always runs 99 per cent copper plus silver, and is not likely to carry more than a few hundredths of a percent of any impurity but nickel. (b) is the old Welsh process, still used to some extent abroad, based upon the reaction between copper oxides and sulphides to eliminate sulphur as sulphur dioxide gas, and carried out in a long series of roasts and fusions in reverberatory furnaces. The removal of impurities is here imperfect, although they may be to a certain extent segregated in a portion of the product, when the origin of the "best selected" copper of Great Britain. When the ores are wholly oxidised the copper may be recovered by direct reduction in a blast furnace (c), and as this is a strictly reducing process the resulting black copper seldom runs over 96 per cent, due to iron and other impurities reduced. Except in the case of "best selected" and similar English coppers all of the products from the foregoing processes are given a further treatment or refining which may be broadly divided into furnace or fire refining and electrolytic refining.

Fire refining is based upon the scorifying effect of cuprous oxide upon base metals contained in a bath of molten copper. The crude copper is melted in a reverberatory furnace, and air blown into the bath. Cuprous oxide rapidly forms and dissolves in the bath, the blowing being stopped at or before the saturation point. In this way oxygen is carried to all parts of the molten bath, and when there are any metals present which are more easily oxidised than copper, cuprous oxide is reduced back to copper, and the oxide of the impurity is formed. If

this oxide is not soluble in the molten copper it will float to the surface, where it may be removed by skimming. As copper stands high among metals in the order of nobility the metallic impurities with the exception of the precious metals may be readily removed in theory. In practice while elimination proceeds rapidly while considerable quantities of impurities are present, the rate diminishes until traces are reached which cannot be slagged off with any reasonable amount of scorifying. Therefore furnace refining is limited in its application to relatively pure crude copper unless a low grade refined copper is contemplated. Less than 10 dols. worth of silver and gold per ton will justify electrolytic refining.

Returning to the bath of molten copper which has been skimmed clean, it is necessary to reduce the excess cuprous oxide dissolved, and no better way has yet been devised than the old Welsh process of covering the bath with a protecting layer of charcoal or low sulphur coke, and then forcing the butts of green trees or poles of hard wood beneath the surface by means of suitable tackle. The cuprous oxide is reduced in this way until a normal amount corresponding to an oxygen content of from 0.04 to 0.07 per cent is left when the copper develops its best physical characteristics, the condition of the copper being followed by the appearance of the fracture of small buttons cast in a spoon or "say ladle" which is a sort of ductility test, and by the swell or depression of the surface of an ingot as it cools, which indicates the gas content. The copper is then cast by means of one of the several types of lading machines which have been very successfully developed in recent years.

When the copper is to be electrolytically refined it is first given a rough furnace refining and cast into anode plates, which are then electrolysed in a strongly acid solution of copper sulphate. The same order of nobility applies, but the great preponderance of copper over the impurities is now an aid as it assists the selective action of the current in depositing only copper at the cathode. Silver and gold are also saved as they are insoluble in the electrolyte chosen, and fall to the bottom of the tank as anode mud or slimes to be separately refined and parted. It is quite evident that copper entering an electrolytic refinery must entirely lose its identity, and that the purity of the resulting cathode copper will depend upon the conditions under which electrolysis is carried out rather than upon the momentary quality of the day's anodes. Therefore it is not necessary to consider whether the input be converter bar, black copper, or Lake mineral when buying electrolytic, but simply whether the product meets the accepted standards of quality for electrolytic copper.

Electrolytic cathodes should be very pure. They generally run about 99.95 per cent copper, much of the missing 0.05 per cent probably being hydrogen. The metallic impurities generally total about 0.02 per cent. Except for the fact that individual cathodes may vary more or less in impurity content they are ideal material for brass making. Copper producers, however, have never encouraged the sale of cathodes, as there is apt to be some shrinkage in weight during shipment owing to the comparative ease with which nodules or small pieces can be detached either accidentally or intentionally. Also cathode shipments unbalance the work in a refinery in proportion to their magnitude, as melting cathodes into market shapes is a distinct part of the process.

This melting is done in a reverberatory furnace, and originally was an exact duplication of the fire refining already described. As the cathode copper is already pure, a simple melting is all that should be required, but molten copper is so susceptible to contamination that until recently the gases from combustion, iron in the rables, &c., were absorbed to a sufficient extent to require actual refining. At the present time large quantities of cathodes are being added to the molten charge during lading and earlier, basic furnaces are being substituted for acid ones, thereby suppressing slag formation, and attention is being paid to keeping coal ashes from blowing over from the

\* Paper presented at the Annual Meeting of the American Institute of Metals, Sept. 7 to 11, 1914, at Chicago, Ill. From the *Chemical Engineer*, xx., No. 5.

firebox, so that a true melting without refining is being approached.

It is well known that cathode copper when drawn into wire will show an electrical conductivity some 2 per cent higher than the same copper after a subsequent fire refining. This is probably due partly to the fact that chemical impurities in the cathode are chiefly present as a mechanical mixture due to adherence of anode slimes which are dissolved in the copper when melted, making a high resistance matrix around the copper crystals when the metal is cast and cooled, and partly to contamination during melting. It seems probable that the conductivity of perfectly pure soft copper is in the neighbourhood of 103 per cent of the Matthiessen standard in common use.

Lake ores are low grade native copper deposits, which are mechanically concentrated to an 85 per cent mineral. This is melted, and, after skimming off the slag formed by the remaining gangue, is given a fire refining as previously described. The Michigan mines are among the oldest, largest, and deepest in the world. Thirty years ago Lake copper was the standard of the industry. The surface ores were remarkably free from objectionable impurities, and copper of the highest conductivity was readily produced. The first electrolytic copper to come on the market was of irregular character due to lack of familiarity with the principles of this new process, and for a considerable time Lake copper was deservedly considered superior. With increasing depth, however, many of the mines showed increasing quantities of arsenic, and, indeed, all Lake copper may be considered as arsenical copper, although in some brands the arsenic is very low. The result was that electrolytic copper began to take precedence for electrical work, as its conductivity could be absolutely depended upon, and Lake began to fall back upon superior "working" qualities, a term which defied exact definition.

It is now generally admitted that high conductivity Lake copper cannot be distinguished from electrolytic copper, while low conductivity Lake is really an alloy of copper with arsenic which has certain desirable properties for special uses. Nearly all the elements which markedly depress the conductivity when alloyed with copper are helpful in developing desirable mechanical properties; for example, phosphorus, aluminium, and silica. High arsenical copper running about 0.4 per cent arsenic has now a special market for making firebox plates in Germany, and uses are beginning to be found for the intermediate grades. One of the large Lake companies maintains its own electrolytic refinery, and in this way recovers a small amount of silver, and eliminates the arsenic, the product still being classed on the market as Lake, although it is equally electrolytic. The old prejudice in favour of Lake on general principles has now largely died out, but only with the contemporaneous retirement of the older generation of wire mill managers. Lake copper should be clearly graded by arsenic contents into a series of alloy coppers, the class at one end competing with electrolytic on its own ground, and the other classes sold in competition with arsenical copper from other sources, a field which has only lately been properly appreciated.

The last class of copper produced which we have to consider is that generally known as casting copper, a very loose term covering a multitude of sins. There are three main sources of casting copper:—(a) From converter bar or black copper from smelters whose ore supply carries quantities of silver and gold insufficient to pay for refining, (b) by-product copper not up to standard electrolytic grade occasionally produced by refineries, and (c) the result of smelting scrap reclaimed from all sorts of new and old work. The first is often of excellent quality, one well-known brand being maintained at 99.80 per cent Cu or better, and is generally comparable with English best selected. The second class is generally an arsenical copper, and is not now often seen as the refineries are nowadays able to eliminate arsenic from the process in other ways. The third class is generally foul, but often

suitable for common castings as the impurities help the founding, pure copper being a difficult metal to handle in a foundry. The copper contents may run below 99 per cent Cu however.

Specifications for Lake and electrolytic copper may be readily drawn, and after a thorough investigation the American Society for Testing Materials has issued a set which should be generally accepted by engineers, as it has already been by the large refineries and wire mills. Casting copper presents a specification problem hopeless of solution at the present time, as there are well-known brands in the market with the widest imaginable range of impurities, all of which are being kept consistently within a certain range of quality for each individual brand, and which find a market for various special uses. About the one thing that can be said of casting copper is that neither a conductivity nor a ductility test is applicable in the nature of things.

Turning now to the uses for copper, they may be broadly classified as follows:—(a) Wire and other shapes for electrical purposes; (b) sheets and plates for non-electrical uses; (c) copper castings, generally for electrical use; (d) in alloys such as brass and bronze; (e) special purposes for which small quantities of alloyed impurities may be advantageous.

Electrical use immediately imposes a conductivity requirement which rules out everything but electrolytic and high conductivity Lake, which, as before stated, are practically identical coppers. Most of the electrolytic refineries figure on averaging about 100.0 per cent soft in the electrical conductivity of their outputs. Occasional lots may reach nearly to 101.0 per cent, and some may approach 99.0 per cent, while 98.5 per cent is the usual rejection limit, but it is very unusual for a refinery to ship anything for electrical use which is below 99.0 per cent. No distinction is made between cakes, wire bars, and ingots, more than one shape often being cast from a single furnace charge, so that there is nothing to be gained by ordering wire bars and then cutting them up when ingots are desired. Unless electrical use is specified it is customary to allow an additional leeway of 1 per cent in conductivity to the refiner, but he rarely needs this, and prefers to maintain the higher standard, as copper is often re-sold several times before it comes into the hands of the actual user. As copper from a single furnace charge will carry practically uniform chemical impurities, shipments on an individual order should be filled from as few furnace charges as possible, and all wire bars and cakes should be stamped with marks identifying these charges. The refiner will always consider complaints on a furnace charge basis if they are of a chemical nature. If they are indefinite he will generally investigate what other customers received copper from the charge complained of, and in the absence of other complaints will demand a bill of particulars before giving the matter serious consideration. The conductivity of a furnace charge is generally determined at the refinery several times while the charge is being cast, and this precaution together with the ample margin above rejection limits which is maintained have practically abolished conductivity complaints.

When copper is not to be put to an electrical use conductivity is of no special value except as a certificate of the absence of more than a trace of a certain class of impurities. The refiner divides impurities into three classes; those that depress conductivity, such as arsenic and antimony; those that impair ductility, such as lead, tellurium, and bismuth; and those which are of value if reclaimed, such as silver, gold, platinum, and palladium. The elements which depress conductivity are kept within bounds by the conductivity test regularly made. Those which are of value if reclaimed will never reach quantities sufficient to affect the physical properties of the copper as it would pay to re-refine any such copper. The remaining class comprising elements which impair ductility is more difficult to deal with.

We know that bismuth, lead, tellurium, and probably

selenium make copper very brittle even when present in very small quantities. We do not know, however, how to write a specification limiting these impurities, as the presence of small amounts of other impurities will neutralise their bad effects. We do not know that amounts of lead up to 0.0005 per cent have no perceptible effect in mill practice or in alloys. Double this amount shows mild effects. Lead is about the only one of the group ever met with in sufficient quantity to be of interest. As these elements are practically insoluble in copper their effect on the conductivity is directly proportional to the amount present and consequently negligible.

It must be understood that an element like lead is always present in small amounts in refined copper, and the mere fact of its presence as shown by a delicate qualitative test is no basis for complaint. It should be further borne in mind that the determination of the small quantities of impurities in refined copper quantitatively can only be done with even reasonable accuracy by a chemist who has had large experience in this particular work. A representative analysis of refined electrolytic copper would be somewhat as follows:—

	Per cent.
Conductivity (annealed) ..	100.0
Copper .. .. .	99.93000
Silver .. .. .	0.00100
Gold .. .. .	0.00001
Sulphur .. .. .	0.00300
Oxygen .. .. .	0.04000
Iron .. .. .	0.00350
Nickel .. .. .	0.00400
Arsenic .. .. .	0.00200
Antimony .. .. .	0.00300
Aluminium .. .. .	0.00100
Phosphorus .. .. .	Trace
Lead .. .. .	0.00200
Bismuth .. .. .	Trace
Selenium .. .. .	0.00050
Tellurium .. .. .	0.00050
	99.99051

It will be seen that oxygen is the chief impurity. It has been pretty conclusively shown that too much oxygen makes the copper harder, and affects the annealing temperature, the tensile strength of wire, and the number of breaks in a wire machine. This may be due to some surface effect, as the "set" surface of a wire bar has a greater oxygen content than the body of the bar, and as the oxygen content increases it is possible that this oxidised layer becomes thicker. Another point about high oxygen is that it corresponds to low copper contents, and to that extent is sold as copper. In brass making the "set" or "pitch" of the ingot is of no consequence except when the most careful work is done when melting in the foundry to avoid further absorption of oxygen. It is obviously useless to impose rigid conditions upon the refiner if the same conditions are not observed in the remelting, and it is only at the largest and best equipped brass foundries that such conditions are even approached. When zinc is introduced into molten copper it acts as a deoxidising agent forming zinc oxide. If the copper is kept at very high pitch this source of zinc loss and dirty brass can be greatly diminished, and this fact has resulted in a demand for high copper contents in ingots. It has therefore become a general custom to specify that the copper contents of refined copper shall not be less than 99.88 per cent, which really means 99.90 per cent, allowing 0.02 per cent for assay variations. As this is a rejection point the actual average content is expected to be between 99.92 and 99.94 per cent.

When we come to casting copper a far greater leeway must be allowed as already pointed out. In fact, except in considering the price charged for the material, copper contents have but little to do with casting copper. It is best to buy this material on the basis of known brands

after finding what brands yield good results in the particular class of work and then insist upon uniform deliveries, judging the material by chemical analysis of the chief impurities.

The physical defects of refined copper are many. Practically all cast copper is porous, doubtless due to the discharge of dissolved gases as the copper cools.

This is analogous to the "piping" of steel ingots, but is not so pronounced because copper is cast in a shallow mould instead of on end. These microscopic bubbles are doubtless the cause of roughness in wire. Then there is a class of defects inseparable from ladling, consisting of cold sets and splashes where the copper has run up on the mould, and chilled before the main body of metals reaches that point. Then there is porosity or sponginess of the surface due to the mould being either too hot or too cold. Another defect is raised edges on the set surface, generally due to slightly lowered pitch corresponding to excessive oxygen content of the copper. Should the pitch drop still lower "nigger heads" or little black spots will appear. These are the outlets of gas cavities extending some distance into the copper. On the other hand, should the oxygen content be too low the surface of the bar rises, and finally breaks open or "spews," an even worse condition.

Many of these defects are always present in more or less degree. Mechanically ladled copper can never be perfect. Specifications require that copper shall be free from mechanical defects, but a reasonable attitude regarding minor troubles on individual pieces is generally necessary to the peace of mind of a buyer. On the other hand, a refinery occasionally becomes careless in such matters, and will send out some surprisingly bad work, so that careful systematic inspection combined with an attitude of friendly criticism is the best way for a copper producer and a copper user to live together.

## WHY AMERICA DOES NOT MANUFACTURE ANILINE DYES.\*

By HARRY McCORMACK.

THERE has been so much written and said during the past few weeks on the subject of aniline dye manufacture that it will probably be difficult to present any new ideas to you. If this is the case, permit me, at least, to hope that the old ideas may be given a new setting.

It has seemed to the speaker that some of the reasons which have been advanced as fundamental ones for our not engaging extensively in the aniline dye industry are at best only contributory causes, and are not fundamental at all.

Any one who is a student of economic conditions has observed that there are certain stages in the industrial development of all countries, the stages commencing with the simple industries carried on by a people subduing a virgin land, when the manufacturing industries are limited to those essential for existence, and progressing slowly toward the stage where the industries are extremely diversified, with the raw materials available worked up into the most finished products.

This country as yet can be said to be in the early stages of industrial development. Our energies and financial capital have been employed to the limit in such labours as the construction of our railway systems, the building of our large cities, the constructing and operating of street railway systems, waterworks, gas and electric plants, and numerous other utilities which must enter into the growth and life of a new country which is attempting to take on all of the improvements of an advanced civilisation.

\* Paper read at the November meeting of the Chicago Section of the American Chemical Society. From the *Chemical Engineer*, xz., No. 6.

These lines of industry, it has been said, afforded ample opportunity for investment, such investments being secure both as regards principal and as to returns on principal. While such opportunities for investment are available, capital will be very slow to invest in any new lines, particularly such lines as chemical industries which are not very well known in this country, and on this account not very well considered as investments by our capitalists. About the only opportunity a chemist has to secure capital for investment is to bring forward some marvellous and secret process to extract gold from sea water, or some process for securing platinum from black sands, or some other project based on imagination.

The development of our railways and public utilities has by no means reached its limit, still affording an opportunity for the investment of our surplus capital, together with much capital coming from European countries. It will therefore be some time before much capital is available for investment in chemical industries.

The mental viewpoint of our nation as a whole has been a handicap to the development of the chemical industry. As a nation we are hasty and impatient. We are not so constituted that we can spend years of research on particular problems, as has been the case with the men who have been most successful in bringing forward new chemical processes. Our chemists mainly are desirous of working at problems promising quick solution. Our chemists, too, seem to prefer to work on problems which have no utilitarian possibilities. The idea seems to be that it is a disgrace to secure any money for scientific achievement. The chemist has his mind fixed on some "real contribution to chemical knowledge," with the idea that any "real contribution to chemical knowledge" can be of no practical value. Our American capitalist, seeking immediate returns on his investment, has, on the other hand, the dollar under such close focus that only a high power objective can be used which produces very high magnification. It is therefore extremely difficult to bring these two parties, chemist and capitalist, together, and have them work for the common good.

All industries in this country, chemical as well as others, are still suffering from the idea on the part of the practical man that the scientist possibly may be of use to teach his theory to someone who has no more important work than to learn this theory, but can be of no possible use to the practical man. On the other hand, the scientist has a poor opinion of the brains of the practical man, thinking that by accident he has been able to accumulate some money, but so far as being of any practical value to the world—certainly not. He has contributed nothing to the advancement of human knowledge. The attitude of both must change, and each must be willing to admit the need of the other before we can secure the desired industrial advancement.

This viewpoint in some of the European countries, particularly in Germany, is radically different. The chemist in Germany is looked on as one of, if not the principal, contributor to the commercial success of the nation. Everything possible is done to aid him in his work. There is a close connection in Germany between the college professor or instructor and the establishment having the need of expert chemical knowledge and advice. Indeed, many of the men connected with large universities are also engaged in research problems brought up by some manufacturing establishment. They receive from their college connections sufficient salary to enable them to live, and receive from the manufacturing establishment a small salary, with the understanding that when any processes are brought out of commercial value a portion of the proceeds will go to the discoverer. This arrangement, it is believed, has contributed more than any other one thing to the success of Germany in the establishment and enlargement of all her chemical industries, particularly of the aniline dye industry.

While we are speaking of the aniline dye industry and commenting on Germany's success in this line

of chemical endeavour, we must not forget that the aniline dye industry originated in England, and that for several years England enjoyed a monopoly of this business. Perkin, an English chemist, in 1856 prepared the first colouring material from coal-tar. The first colour prepared was mauve. This was followed by a number of others brought out in different years, extending from 1856 up to about 1867. All of these dyes were new materials, so were not attempts in any way to duplicate colouring materials at that time on the market, the principal dye stuffs at this time being of vegetable origin, and none of them being prepared synthetically.

The two chief vegetable dyes in use at this time were alizarin, prepared from madder, and indigo, prepared from the indigo plant. About 1869 the Germans commenced to be interested in the production of synthetic dyes. Unlike the English, they were not content in preparing new dyes which would find probably a very limited market, at least for some time. They, however, attempted the synthesis of the dyes which were then most in demand. Graebe and Liebermann in 1869 succeeded in synthesising alizarin, starting with anthracene as the raw material. This dye stuff, when put on the market, of course had to meet at once the strong competition of naturally prepared alizarin. Their work, however, has been so thoroughly done that it was able to meet this competition, and the sales of the natural product fell off very rapidly.

Following the success of these investigators on the synthesis of alizarin came the work of Baeyer on indigo. About 1880 Baeyer had succeeded in synthesising indigo. His indigo synthesis at this time, however, was not a success, as his raw materials were too costly and the yield too low. He was, however, able to sell his patents to the Badische Anilin Company for about 100,000 dols., and from these patents they received no practical benefit. This, however, did not deter them from purchasing in 1890 the patents of Heumann for the synthesis of indigo, starting with different raw materials and conducting the synthesis in a different manner. Heumann's synthesis enabled the manufacturers to make use of naphthalene, a very cheap and abundant coal-tar product, as a basis for their indigo synthesis. It is true, however, that the first step in the production of indigo from naphthalene was not brought out in the original process, but was discovered some years later. Long years of experimenting on the part of these German chemists was rewarded by the successful commercial outcome of both of these syntheses on alizarin and on indigo. Practically both the natural products have been driven from the market by the artificial ones.

England, who commenced the manufacture of these coal-tar dyes, has lost this business to such an extent that we hardly think of England as entering into the production of coal-tar dyes at all.

There must, therefore, be some reason why England lost this supremacy. We are accustomed to think of Germany as being the originator of the industry, but, as has been shown, this is not true. It is the writer's opinion that the prime reason for England losing this great industry is the fact that she had no connection between the industries and the university man as Germany has developed; therefore, not having the available research talent which is absolutely necessary, no new processes or materials were brought out, and the industry therefore died. We, like England, have no such body of research men at the present time who would be available for research service along the lines desired.

Lack of raw materials in this country is also an additional reason why we have no considerable aniline dye industry. With all the other things which are necessary in the building up of a coal-tar dye industry, we must have some coal-tar. So long as we persist in coking 85 per cent of our coal in beehive ovens, where the volatile products are entirely lost, just so long will we lack the necessary quantity of coal-tar products for the establishment of the aniline dye industry. In the manufacture of aniline



dyes it is necessary that we not only have coal-tar, but that we have coal-tar in very large quantities. Hausermann estimates that 100 kilogrammes of tar under distillation will yield:—

- 0.6 kilogram. of benzene.
- 0.4 kilogram. of toluene.
- 0.5 kilogram. higher homologues of benzene and toluene.
- 8 to 12 kilogramms. of naphthalene.
- 5 to 6 kilogramms. of phenol.
- 0.25 to 0.30 kilogram. of anthracene.

The above would represent products obtained from the coking of 2000 kilogramms. of coal. It should also be stated that in the distillation of the tar we get about 30 per cent creosote oils and about 60 per cent pitch. Both of these products must also be commercially utilised if the handling of the coal-tar is to be profitable.

We must remember, when we are considering the aniline dye industry, that it is an industry which deals not only with the products obtained from coal-tar, but that it is a very widely diversified chemical industry. Before these products, obtained from the distillation of coal-tar, are available in any way as dye stuffs, they must undergo many chemical transformations, and many chemicals will be necessary in order to bring about these transformations. We find therefore that the great German aniline dye companies are also very extensive manufacturers of practically all kinds of chemicals.

You are doubtless familiar with the fact that a group of these German companies went to Norway several years ago and purchased the plant and rights of the company operating the Rirkeland-Eyde patents, and commenced the manufacture of nitric acid from the air. You possibly may also be familiar with the developments in this direction since this time; that these companies have developed the greatest group of hydro-electric plants in the world, and have gone into the manufacture of nitric acid, calcium nitrate, sodium nitrite, calcium carbide, and calcium cyanamide on a scale never before attempted. These Norwegian projects alone have an actual investment of upwards of fifty million dollars.

It is estimated by one of our best informed American dye manufacturers that it would take at least 400,000,000 dols. to cover the investment in Germany of various German companies engaged in aniline dye manufacture. This gives you some idea of the capital involved in the industry.

To obtain an adequate idea of the industry you should realise, in addition to the amount of capital invested, something of the *spirit* which these men have invested in their industry. This can possibly be best visualised by calling to your attention some of the recent achievements of these two companies. One of them, as you will remember, recently brought out the synthesis of ammonia after Haber and Le Rossignol had worked on the problem for some ten years in spite of the fact that it had been previously said by many chemists to be unsolvable. The other company, you will remember, gave us the process for the synthesis of rubber, this process being worked out completely to a satisfactory conclusion possibly years before there will be a real commercial demand for their product. You must remember that to have real commercial demand for a product it must be sold at a price to meet all competition. Here they are bringing out an article which will have to compete in price with the natural rubber. They did not hesitate, however, on this account, but proceeded with their experimental work and developed the product, their previous experiences with alizarin and indigo having shown them that if you work long enough you can succeed in overcoming even such competition as is to be met in outselling a natural product by an artificial one. Some of our American writers in the past few weeks seem to have forgotten that the aniline dye industry in its early history had to overcome such competition in the line of alizarin and indigo, which was much more strenuous than any conditions which would have to be met by

American manufacturers entering the field with aniline dyes. The writer has an impression of the German spirit in chemical industry which will never be effaced: Dr. Bernthsen at the Eighth International Congress of Applied Chemistry, had just concluded his masterly Address on the synthesis of ammonia, when Dr. Duisberg, director of a rival German company, advanced to the platform and proceeded to tell us of the importance of this work and its effects. His attitude was that of a man glorying in the accomplishments of his fellow chemists, even if rivals, and seemed to radiate the feeling that if there was any more important work in the world than that in which he and his associates were engaged he had never heard of it. When we can secure some such attitude as this among our chemists, our industries will not fail to advance.

Probably the best way to present to you some idea of the things required in the manufacture of aniline dye would be to take a typical product such as indigo, and outline to you the steps necessary in the transformation of the coal-tar product to the dye. There are two syntheses being used for the production of indigo; one starting from benzene and the other from naphthalene. As you noted from the table given, naphthalene is much the largest single constituent obtained from coal-tar which is utilisable in dye manufacture. It is therefore the cheapest raw material which can be used for the synthesis of indigo. The process using naphthalene is therefore selected, and the steps are as follows:—

The naphthalene is oxidised to phthalic anhydride by being heated with concentrated sulphuric acid and mercury.

The phthalic anhydride thus obtained is converted into phthalimide by heating with ammonia.

The phthalimide on being treated with bleaching powder gives anthranilic acid.

Anthranilic acid on being treated with chloracetic acid gives phenylglycine-*o*-carboxylic acid.

The phenylglycine-*o*-carboxylic acid fused with sodium hydroxide yields indoxyl.

Indoxyl when treated with a large amount of air blown through the solution oxidises to indigo the product desired.

It is noticed in this table that in the transformation from naphthalene to indigo there are seven operations requiring six different chemicals. A manufacturer to be successful in this industry would have to be able to supply these chemicals from his own factories, and thus be independent in his raw materials. To be successful he would also have to develop a market for the various products he was manufacturing; that is, it would not suffice for him to manufacture these chemicals only in the quantities required in his own plant, but to obtain them economically must manufacture them in large quantities, and be prepared to sell each and every one of them in the open market.

We should not leave the subject of the aniline dye industry without some comment on the conditions in the industry which are peculiar to this industry. First, the manufacturer must produce many different dyes to satisfy his customers. It is estimated that some 900 different dyes are imported into this country. Second, he must be continually seeking for new dyes of different shades and of more satisfactory qualities. The manufacture of dyes in this way is not like the manufacture of, say, steel products. Approximately the same steel products are in style to day as were in style five years ago, but in the dye industry shades which are eminently desired this year may not be marketable at all next year.

Summarising the reason why we do not manufacture aniline dyes, I would state them as follows:—

First, the scarcity of capital available for investment in such industries.

Second, the desire of the American capitalist to secure quick and sure returns on his investments and his inability

0 see 2.00 dols. in the distance where there is 0.50 dol. in the foreground.

Third, lack of co-operation between the colleges and universities and our chemical industries.

Fourth, lack of raw materials, due to our waste of our natural resources.

Fifth, our American characteristics of haste and impatience.

Sixth, unsatisfactory patent laws.

Seventh, low tariff on imported aniline dyes.

## ON THE ACTION OF LEAD, COPPER, TIN NICKEL, ZINC, AND ALUMINIUM ON WATER.

By Dr. W. P. JORISSEN, The University, Leiden, Holland.

(Continued from p. 70).

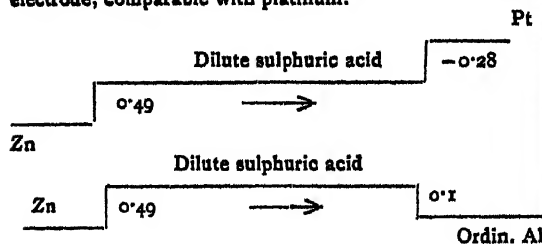
### 9. Aluminium.

ORIGINALLY aluminium had been given a place below zinc, but after Neumann's investigations the order is that which is to be found in the table on page 56, viz., zinc is a "nobler" metal than aluminium (Note 45). Yet several experiments made by Ch. M. van Deventer and H. van Lummel (Note 46) would lead to another conclusion.

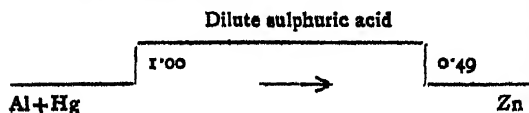
Thus, for instance, ordinary aluminium does not precipitate zinc from a solution of zinc sulphate (which it does from an alkaline one). Ordinary aluminium hardly acts upon dilute sulphuric acid, as is also the case with pure zinc (see *ante*); but when the metals are brought into contact with each other when immersed in the acid a considerable liberation of hydrogen takes place on the aluminium. Aluminium consequently behaves in this respect just like, for instance, copper, silver, gold, or platinum (Note 47), and so it ought to be regarded as "electronegative" to zinc (Note 48). When a galvanic cell is constructed by means of ordinary aluminium, amalgamated zinc, and dilute sulphuric acid, the zinc is found to be the dissolving electrode. Van Deventer and van Lummel found the E.M.F. to be about 0.4 volt; the resistance appeared to be very considerable. In the series of electro-chemical potentials for metals immersed in seawater aluminium must also be placed below zinc (Note 49).

When amalgamated aluminium is taken, however, this metal is able to show its true nature (Note 50); it acts in accordance with its place in the series already given on page 56. Thus, for instance, it precipitates zinc from an ordinary solution of zinc sulphate.

Van Deventer ascribes the abnormal behaviour of the ordinary metal to a film of oxide (Note 51). According to J. J. van Laar (Note 52) this "film of oxide," or whatever it may be (Note 53), prevents the sending out of Al-ions, and therefore the aluminium becomes an ordinary hydrogen electrode, comparable with platinum.



With amalgamated aluminium, however, the behaviour of the metal is reversed, thus—



It is a well-known fact that aluminium remains practically unaltered in dry air (Note 54). In moist air a superficial film of oxide seems to protect the metal from further oxidation (Note 55). The action of water and air has been studied (Note 56) by W. Ohlmüller and R. Heise (Note 57). They observed that distilled water acts only in a slight degree. When a sheet of aluminium (containing 0.053 per cent cryst. Si, 0.45 per cent Si in a combined state, and 0.292 per cent Fe), with a surface of 310 cm<sup>2</sup>, was immersed in 500 cc. of this water, in two days 1.12, in four days 3.15, and in six days 3.79 mgrms. of aluminium were found to be dissolved. Carbonic acid proved to have no perceptible influence. The action of water from the water supply (analysis not given) was also studied. Crater-shaped corrosions were formed, first white, then yellowish. The analysis showed the presence of oxides of Al, Fe, and Ca, the latter in small quantities, and carbonic acid. In nearly all these a small gas bubble was observed, containing oxygen, nitrogen, and hydrogen. On removing the craters, dark, clearly defined, eroded spots remained behind. In 500 cc. of this water 5.4 mgrms. of Al were found after twenty-four and 11.5 (resp. 15.0) mgrms. of this metal after six days).

When the water was practically freed from air by means of an air-pump the craters still appeared.

In a 2 per cent solution of sodium chloride the number of corroded spots was much larger; the craters, however, were very small and not so firm as in the case of the drinking water. In the salt solution soon a voluminous precipitate appeared. After two days 8.56 mgrms., after six days 26.23 mgrms. of Al were found to be present in this solution. Ohlmüller and Heise suppose the metal to possess places consisting of a less resisting alloy; they also consider the possibility of an influence of the manufacturing process which the metal has undergone.

Heyn and Bauer's experiments on the corrosion of aluminium sheets and vessels show that the greater the cold work put on the metal the greater is the tendency to local corrosion.

After annealing at 450° only general corrosion occurs (Note 58).

That sea water acts in about the same way as a 3.2 per cent solution of sodium chloride has been observed by myself (Note 59). After an exposure for weeks in water containing carbonic acid under pressure, a loss of weight of only 0.2 per cent was observed by Neuman Wender (Note 60).

When aluminium is treated with a solution of mercuric chloride, or when the metal is immersed in mercury directly after having been scrubbed, an amalgam is formed. This amalgam readily oxidises. In air containing water vapour and carbonic acid principally aluminium hydroxide (not a definite hydrate) is obtained; however, a carbonate and a peroxide being also formed, according to Jourdain's observations (Note 61).

The fact that aluminium amalgam decomposes water at the ordinary temperature has been used by Mauriceau-Beaupré (Note 62) to work out a process for the manufacturing of hydrogen on a large scale. He adds to the metal small quantities of corrosive sublimate and potassium cyanide. As regards the use of aluminium actified by mercury, reference may be further made to the investigations of Kohn-Abrest (Note 63).

That amalgamated aluminium behaves differently from amalgamated zinc (which does not act upon dilute sulphuric acid) is due to the fact that the electro-chemical potential of aluminium is larger than the overvoltage of mercury (compare Note 9).

Of the other alloys of aluminium, as composed chiefly of this metal, magnalium and duralumin may be mentioned here. The former contains magnesium in varying quantities, and sometimes small quantities of other metals; it is less corrodable than aluminium. The latter (containing 0.5 per cent Mg, 3.5–5.5 per cent Cu, and 0.5–0.8 per cent Mn) is even said to offer a strong resistance to the action of sea water, in contrast with ordinary aluminium (Note 64).

### 10. Zinc.

In pure distilled water, free from dissolved oxygen and carbonic acid, zinc retains its shining surface even for some years (Note 65). However, when oxygen is present oxidation takes place (Note 66). Zinc hydroxide is formed, of which the solubility in water is slight (9 mgrms. per litre, according to A. J. C. Snijders) (Note 67). When air and therefore carbonic acid is present also basic carbonate will be formed; in this case practically the same quantity of zinc is found dissolved in the water (Note 68).

Snijders (Note 69) determined the solubility of zinc hydroxide (formed during the oxidation of zinc in water and air, carbonic acid being absent) in 1 per cent solutions of several salts. The following results in mgrms. Zn per litre were obtained: sodium chloride (temp. 18°) 51 mgrms., calcium chloride (16°) 57.5 mgrms., magnesium chloride (16°) 65 mgrms., ammonium chloride (20°) 95 mgrms., magnesium sulphate (21°) 27 mgrms., potassium carbonate (15°), ammonium nitrate (20°) 77 mgrms., &c.

When he exposed 25 cm<sup>3</sup> of pure zinc in a 1 per cent solution of sodium chloride to the action of air, free from carbon dioxide, he found after fourteen days (temp. 12–18°) about 54 mgrms. of Zn in a litre of the solution and about 14 mgrms. of Zn as precipitate (hydroxide). As in the case of distilled water, 9 mgrms. were found in the solution and 8 mgrms. as precipitate; the rate of oxidation was consequently increased by the salt (Note 70).

When carbonic acid was present he found after fourteen days (temp. 11–16°) about 45 mgrms. Zn in the solution; hence a somewhat smaller quantity than in the case of air free from carbonic acid. If crude zinc was used (Note 71) instead of pure zinc the results did not differ much; the rate of the oxidation was increased a little.

The following results were obtained with 1 per cent solutions of other salts (in fourteen days) (Note 72): Potassium sulphate (12–14°) 85 mgrms. Zn per litre dissolved, 36 mgrms. as precipitate; magnesium sulphate 90 mgrms. dissolved; sodium nitrate (12–16°) 24 mgrms. dissolved, 11 mgrms. precipitate (Note 73); potassium carbonate and sodium hydrocarbonate did not dissolve any zinc, only a film being formed.

Finally, Snijders investigated the action of four different kinds of spring water. Only in one case (where much carbonate was present) no dissolved zinc was found in the water (after fourteen days), a small quantity was observed as precipitate, a film being formed on the metal.

H. Bunte (Note 74) filled galvanised iron tubes (length 3 metres, diameter 50 mm., contents 5.9 litre, inner surface 0.47 m<sup>2</sup>) with water.

After 11.5 days distilled water had dissolved 19 mgrms. Zn per litre, a solution of calcium sulphate 54 mgrms., after three days a solution of sodium chloride (0.4 grm. per litre) 25 mgrms., different kinds of water (analysis not given) after 1–11.5 days 3–11 mgrms.

G. Wolhügel (Note 75) found that the action of water on galvanised iron tubes is dependent on the composition of the water. He concludes that before using such tubes for drinking water, it is necessary to investigate first the action of the water in question (Note 76).

That rain water which comes into contact with zinc roofs, &c., may contain zinc in appreciable quantities need not be stated.

### 11. Nickel.

Nickel has an electro-chemical potential of 0.228 volt in normal solutions of Ni-ions, while its overvoltage in normal solutions of sulphuric acid amounts to 0.21 volt. This accounts for the fact that it acts only slowly on dilute hydrochloric and dilute sulphuric acid.

The circumstance that nickel is not corroded by air and water, not even by sea water, enhances its practical value. Ernst Cohen (Note 77) found that nearly pure nickel of Krupp (99.9 per cent), after having been exposed for four

weeks to the action of sea water and air, had retained its polish and had not in the least been corroded.

Besides a sufficient percentage of nickel (more than 35 per cent) will prevent iron from rusting (Note 78).

### 12. Tin.

Tin is somewhat less "noble" than hydrogen: its electro-chemical potential amounts to less than 0.192 volt; its overvoltage, however, being 0.55 volt in a normal solution of sulphuric acid; it will not liberate hydrogen from dilute sulphuric acid. On the other hand, tin will dissolve in the presence of air, as the hydrogen may be oxidised in that case on the surface of the metal (compare *ante*). It appears, however, that the catalytic action of tin in this respect is smaller than that of lead. Sackur (Note 79), namely, found that in the presence of air only traces of tin dissolve in dilute acetic acid.

That tin will be proof against the action of pure water is therefore to be expected. Thus in making distilled water it is customary to make use of a tin cooling tube.

It is also to be expected that tin, unless impure, will either not dissolve at all, or only in small quantities in water containing carbonic acid when air is absent or nearly absent (Note 80).

That technically pure tin of the kind used as lining in water pipes is acted upon by drinking water has been found by C. P. E. Ribbins and W. D. Gratama (Note 81). J. D. van der Plaats (Note 82) observed in such cases greyish stains and streaks across the tin, consisting of stannous and stannic oxide, mixed with substances deposited from the water. No definite conclusion was arrived at regarding the question whether galvanic action had played a part.

Pure tin (99.96 per cent), according to Ernst Cohen's observations, is rather quickly acted upon by sea water containing air (Note 83). It was known already that the tin of tin-plated condenser tubes, through which sea water flows, is corroded. As the tin layer is very thin (as a rule about 0.02 mm.), it is not to be wondered at that this film does not protect the copper or brass sufficiently against corrosion.

Moreover, when the film does not cover the whole surface, as often happens, a galvanic action between the two metals will take place. A layer of basic salts, however, will soon cover the tin (Note 84).

### Notes.

45. Or: zinc is "electro-negative" to aluminium; or, when zinc and aluminium are combined to form a galvanic cell, aluminium is expected to be the dissolving electrode.

46. *Chem. Weekbl.*, 1907, 771.

47. As to silver and gold, their behaviour in this respect has been known for more than a century (Wollaston, 1801; Ritter, 1805); compare the lecture cited in Note 5.

48. To iron, however, it is found to be "electro-positive."

49. Diegel, *Marine-Rundschau*, 1898, ix., 1485. (See Note 5).

50. Van Deventer, *Chem. Weekbl.*, 1906, 625.

51. Compare the "film of oxide" theory of passivity, already mentioned, and van Deventer and van Lummel's investigations on "leaking" non-conductors (*Chem. Weekbl.*, 1907, 771).

52. *Chem. Weekbl.*, 1908, 125.

53. Compare also G. Schulze, *Ann. d. Phys.*, 1907-1909; Taylor, *Ibid.*, 1909, [4], xxx., 987; *Chem. Weekbl.*, 1910, 303, 312.

54. Just like other metals, even potassium and sodium. This fact has already been pointed out as early as 1872 by J. Ariëns Kappers (Dissertation, Groningen).

55. E. Kohn-Abrest, "Recherches sur l'aluminium," 1911, 38, found in aluminium powder an oxide containing less oxygen than corresponds with the formula Al<sub>2</sub>O<sub>3</sub>.

56. See also, for instance, Ditte, *Comptes Rendus*, 1890, cx., 783, who observed a liberation of hydrogen when

immersing aluminium in boiling water, which does not take place at the ordinary temperature, unless the protective film is removed regularly.

57. *Arb. Kais. Gesundh.*, 1893, amte viii., 377: "Untersuchungen über die Verwendbarkeit des Aluminiums zur Herstellung von Ess-, Trink-, und Kochgeschirren."

58. *Mittel. Konigl. Materialpruf. amt. Gross-Lichterfelde West*, 1911, xxix., 2.

59. *Versl. Marine-Ver.*, 1904.5, 131.

60. *Pharm. Post.*, 1892, 201; cited by Ohlmüller and Heise.

61. *Comptes Rendus*, 1910, cl., 391, 1602.

62. *Comptes Rendus*, 1908, clxvii., 310.

63. *Bull. Soc. Chim.*, 1912.

64. L. M. Cohn, "Tech. Mitteil. ü. Duralumin" (Durener Metallwerke A. G., Düren), 1910.

65. Von Bonsdorff, *Ann. d'Hyg.*, Publ. xvii., 290.

A. J. C. Snijders, "Dissertation," Leiden, 1877, 56, could not find a trace of zinc in the water after fourteen days, and M. Traube, *Ber.*, 1885, xviii., 1881, did not observe any liberation of hydrogen after ten days at the ordinary temperature.

66. Ohlmüller and Heise, *Arb. Kais. Gesund.* (1893), amte viii., 395, who immersed a piece of zinc (surface 400 cm<sup>2</sup>) in 100 cc. of distilled water (temp. 20°), found, after having drawn air through the water during twenty-four hours, that 1.2 mgrms. Zn were dissolved.

67. "Dissertation," p. 58. See also Herz, *Zeit. Anorg. Chem.*, 1900, xxiii., 227.

68. Snijders, *loc. cit.*, p. 59.

69. *Loc. cit.*, p. 67.

70. *Loc. cit.*, p. 71.

71. Containing Pb 0.5—1.2 per cent, C 0.5—1.1 per cent, As 0—0.04 per cent, Cd 0—0.09 per cent, Fe traces—0.07 per cent.

72. Snijders, *loc. cit.*, p. 81.

73. When air and carbonic acid are absent these solutions still attack the zinc; *loc. cit.*, p. 72.

74. *Journ. f. Gasbeleucht.*, 1887, Hefte 3-5.

75. *Arb. Kais. Gesundh.*, 1887, amte ii., 174.

76. See also for the use of galvanised iron tubes or zinc tubes for water supply purposes: O. Kröhnke, *Journ. f. Gasbeleucht.*, lv., 421, and Heyn and Bauer, *Mitt. Materialpruf. amt Gross-Lichterfelde West*, xxx., 101; both of which publications I have not been able to read till now.

77. *De Ingenieur*, 1901, 183.

78. Compare Guertler and Tammann, *Zeit. Anorg. Chem.*, 1905, xlv., 205.

79. *Arb. Kais. Gesundh.*, 1905, amte xxii., 205. The tendency to corrosion by dilute acids of lead-tin alloys increases with the percentage of the lead. Primarily it is chiefly lead that is dissolved.

80. Vide, e.g., soda-water apparatus.

81. *Verslag. alg. verg. v. Waterl. belang*, 1900, 35.

82. *Versl. Gezondh. Comm.*, Utrecht, 1902; *Versl. alg. verg. Ver. v. Waterl. bel.*, 1902, 60.

83. *De Ingenieur*, 1901, xvi., 182. From my own observations it follows that a 3.2 per cent solution of sodium chloride acts more quickly.

84. *Ibid.*, p. 183.

(To be continued).

Iron and Steel Institute.—The Annual Meeting will be held by kind permission at the Institution of Civil Engineers, Great George Street, London, S.W., on Thursday and Friday, May 13 and 14, 1915. The date of Thursday, May 13, has been provisionally fixed for the Annual Dinner, and a further announcement will be made if it is found possible for the Dinner to take place. It has been provisionally decided to hold the Autumn Meeting in London during the week ending September 25, 1915.

## SOME ASPECTS OF INDUSTRIAL CHEMISTRY.\*

By L. H. BAEKELAND, Sc.D.

(Continued from p. 67).

Now let us see how Germany won her spurs in chemical engineering as well:—

At the beginning, the manufacturing problema in organic chemistry involved few, if any, serious engineering difficulties, but required, most of all, a sound theoretical knowledge of the subject; this put a premium on the scientist, and could afford, for awhile at least, to ignore the engineer. But when growing developments began to claim the help of good engineers, there was no difficulty whatsoever in supplying them, nor in making them co-operate with the scientists. In fact, since then, Germany has solved, just as successfully, some of the most extraordinary chemical engineering problems ever undertaken, although the development of such processes was entered upon at first from the purely scientific side.

In almost every case, it was only after the underlying scientific facts had been well established that any attempt was made to develop them commercially.

Healthy commercial development of new scientific processes does not build its hope of success upon the co-operation of that class of "promoters" which are always eager to find any available pretext for making "quick money," and whose scientific ignorance contributes conveniently to their comfort by not interfering too much with their self-assurance and their voluble assertions. The history of most of the successful recent chemical processes abounds in examples where, even after the underlying principles were well established, long and costly preparatory team-work had to be undertaken; where foremost scientists as well as engineers of great ability had to combine their knowledge, their skill, their perseverance, with the support of large chemical companies, who, in their turn, could rely on the financial backing of strong banking concerns, well advised by tried expert specialists.

History does not record how many processes thus submitted to careful study were rejected because, on close examination, they were found to possess some hopeless shortcomings. In this way, numerous fruitless efforts and financial losses were averted, where less carefully accumulated knowledge might have induced less scrupulous promoters to secure money for plausible but ill-advised enterprises.

In the history of the manufacture of artificial dyes, no chapter gives a more striking instance of long assiduous and expensive preliminary work of the highest order than the development of the industrial synthesis of indigo. Here was a substance of enormous consumption which, until then, had been obtained from the tropics as a natural product of agriculture. Prof. von Baeyer and his pupils, by long and marvellously clever laboratory work, succeeded by-and-by in unravelling the chemical constitution of this indigo dye, and finally indicated some possible methods of synthesis. Notwithstanding all this, it took the Badische Aniline and Soda Fabrik about twenty years of patient research work, carried out by a group of eminent chemists and engineers, before a satisfactory method was devised by which the artificial product could compete in price and in quality with natural indigo.

Germany, with her well administered and easily enforceable patent laws, has added, through this very agency, a most vital inducement for pioneer work in chemical industries. Who otherwise would dare to take the risk of all the expenses connected with this class of creative work? Moreover, who would be induced to publish the result of his discoveries far and wide throughout the whole world in that steadily flowing stream of patent literature, which, much sooner than any text-books or periodicals, enables one worker to be benefited and to be inspired by the publication of the latest work of others?

\* The Chandler Lecture, Columbia U.S.A., 1914.

The development of some problems of industrial chemistry has enlisted the brilliant collaboration of men of so many different nationalities that the final success could not, with any measure of justice, be ascribed exclusively to one single race or nation; this is best illustrated by the invention of the different methods for the fixation of nitrogen from the air.

This extraordinary achievement, although scarcely a few years old, seems already an ordinary link in the chain of common current events of our busy life, and yet the facts connected with this recent conquest reveal a modern tale of great deeds of the race—an Epos of Applied Science.

Its story began the day when chemistry taught us how indispensable are the nitrogenous substances for the growth of all living beings.

Generally speaking, the most expensive foodstuffs are precisely those which contain most nitrogen; for the simple reason that there is, and always has been, at some time or another, a shortage of nitrogenous foods in the world. Agriculture furnishes us these proteid- or nitrogen-containing bodies, whether we eat them directly as vegetable products, or indirectly as animals which have assimilated the proteids from plants. It so happens, however, that by our ill-balanced methods of agriculture we take nitrogen from the soil much faster than it is supplied to the soil through natural agencies. We have tried to remedy this discrepancy by enriching the soil with manure or other fertilisers, but this has been found totally insufficient, especially with our methods of intensive culture—our fields want more nitrogen. So agriculture has been looking anxiously around to find new sources of nitrogen fertiliser. For a short time an excellent supply was found in the guano deposits of Peru; but this material was used up so eagerly that the supply lasted only a very few years. In the meantime the ammonium salts recovered from the by-products of the gasworks have come into steady use as nitrogen fertiliser. But here again the supply is entirely insufficient, and during the later period our main reliance has been placed on the natural beds of sodium nitrate which are found in the desert regions of Chile. This has been, of late, our principal source of nitrogen for agriculture, as well as for the many industries which require saltpetre or nitric acid.

In 1898, Sir William Crookes, in his memorable presidential address before the British Association for the Advancement of Science, called our attention to the threatening fact that, at the increasing rate of consumption, the nitrate beds of Chile would be exhausted before the middle of this century. Here was a warning—an alarm call—raised to the human race by one of the deepest scientific thinkers of our generation. It meant no more nor less than that before long our race would be confronted with nitrogen starvation. In a given country, all other conditions being equal, the abundance or the lack of nitrogen available for nutrition is a paramount factor in the degree of general welfare or of physical decadence. The less nitrogen there is available as food-stuffs, the nearer the population is to starvation. The great famines in such nitrogen deficient countries as India and China and Russia are sad examples of nitrogen starvation.

And yet nitrogen, as such, is so abundant in nature that it constitutes four-fifths of the air we breathe. Every square mile of our atmosphere contains nitrogen enough to satisfy our total present consumption for over half a century. However, this nitrogen is unavailable as long as we do not find means to make it enter into some suitable chemical combination. Moreover, nitrogen was generally considered inactive and inert, because it does not enter readily in chemical combination.

Sir William Crookes's disquieting message of rapidly approaching nitrogen starvation did not cause much worry to politicians—they seldom look so far ahead into the future. But, to the men of science, it rang like a reproach to the human race. Here, then, we were in possession of an inexhaustible store of nitrogen in the air, and yet, unless we found some practical means for tying some of it

into a suitable chemical combination, we would soon be in a position similar to that of a shipwrecked sailor, drifting around on an immense ocean of brine, and yet slowly dying for lack of drinking water.

As a guiding beacon there was, however, that simple experiment, carried out in a little glass tube, as far back as 1785, by both Cavendish and Priestley, which showed that if electric sparks were passed through air the oxygen thereof was able to burn some of the nitrogen and to engender nitrous vapours.

This seemingly unimportant laboratory curiosity, so long dormant in the text-books, was made a starting point by Charles S. Bradley and D. R. Lovejoy, in Niagara Falls, for creating the first industrial apparatus for converting the nitrogen of the air into nitric acid by means of the electric arc.

As early as 1902, they published their results as well as the details of their apparatus. Although they operated only one full-sized unit, they demonstrated conclusively that nitric acid could thus be produced from the air in unlimited quantities. We shall examine later the reasons why this pioneer enterprise proved a commercial success; but to these two American inventors belongs undoubtedly the credit of having furnished the first answer to the distress call of Sir William Crookes.

In the meantime many other investigators were at work at the same problem, and soon from Norway's abundant waterfalls came the news that Birkeland and Eyde had solved successfully, and on a commercial scale, the same problem by a differently constructed apparatus. The Germans, too, were working on the same subject, and we heard that Schoenherr, also Pauling, had evolved still other methods, all, however, based on the Cavendish-Priestley principle of oxidation of nitrogen. In Norway alone, the artificial saltpetre factories use now, day and night, over 200,000 electrical horse-power, which will soon be doubled; while a further addition is contemplated which will bring the volume of electric current consumed to about 500,000 horse-power. The capital invested at present in these works amounts to 27,000,000 dols.

Frank and Caro, in Germany, succeeded in creating another profitable industrial process whereby nitrogen could be fixed by carbide of calcium, which converts it into calcium cyanamide, an excellent fertiliser by itself. By the action of steam on cyanamide, ammonia is produced, or it can be made the starting point of the manufacture of cyanides, so profusely used for the treatment of gold and silver ores.

Although the synthetic nitrates have found a field of their own, their utilisation for fertilisers is smaller than that of the cyanamide; and the latter industry represents, to-day, an investment of about 30,000,000 dols., with three factories in Germany, two in Norway, two in Sweden, one in France, one in Switzerland, two in Italy, one in Austria, one in Japan, one in Canada, but not any in the United States. The total output of cyanamide is valued at 15,000,000 dols. yearly, and employs 200,000 horse-power, and preparations are made at almost every existing plant for further extensions. An English company is contemplating the application of 1,000,000 horse-power to the production of cyanamide and its derivatives, 600,000 of which have been secured in Norway and 400,000 in Iceland.

But still other processes are being developed, based on the fact that certain metals or metalloids can absorb nitrogen, and can thus be converted into nitrides; the latter can either be used directly as fertilisers or they can be made to produce ammonia under suitable treatment.

The most important of these nitride processes seems to be that of Serpek, who, in his experimental factory at Niedermorschweiler, succeeded in obtaining aluminium nitride in almost theoretical quantities, with the use of an amount of electrical energy eight times less than that needed for the Birkeland Eyde process and one-half less than for the cyanamide process, the results being calculated for equal weights of "fixed" nitrogen.



A French company has taken up the commercial application of this process which can furnish, besides ammonia, pure alumina for the manufacture of aluminium metal.

An exceptionally ingenious process for the direct synthesis of ammonia, by the direct union of hydrogen with nitrogen, has been developed by Haber in conjunction with the chemists and engineers of the Badische Anilin and Soda Fabrik.

The process has the advantage that it is not, like the other nitrogen-fixation processes, paramountly dependent upon cheap power; for this reason, if for no other, it seems to be destined to a more ready application. The fact that the group of the three German chemical companies which control the process have sold out their former holdings in the Norwegian enterprises to a Norwegian-French group, and are now devoting their energies to the commercial installation of the Haber process, has quite some significance as to expectations for the future.

The question naturally arises—Will there be an over-production and will these different rival processes not kill each other in slaughtering prices beyond remunerative production?

As to over-production, we should bear in mind that nitrogen fertilisers are already used at the rate of about 200,000,000 dols. worth a year, and that any decrease in price, and, more particularly, better education in farming, will probably lead to an enormously increased consumption. It is worth mentioning here that, in 1825, the first shipload of Chile saltpetre which was sent to Europe could find no buyer, and was finally thrown into the sea as useless material.

Then again, processes for nitric acid and processes for ammonia, instead of interfering, are supplementary to each other, because the world needs ammonia and ammonium salts, as well as nitric acid or nitrates.

It should be pointed out also, that ultimately the production of ammonium nitrate may prove the most desirable method so as to minimise freight; for this salt contains much more nitrogen to the ton than is the case with the more bulky calcium-salt under which form synthetic nitrates are now put into the market.

Before leaving this subject let us examine why Bradley and Lovejoy's efforts came to a standstill where others succeeded.

First of all the cost of power at Niagara Falls is three to five times higher than in Norway, and although at the time this was not strictly prohibitive for the manufacture of nitric acid, it was entirely beyond hope for the production of fertilisers. The relatively high cost of power in our country is the reason why the cyanamide enterprise had to locate on the Canadian side of Niagara Falls, and why, up till now, outside of an experimental plant in the South (a 4000 horse-power installation in North Carolina, using the Pauling process), the whole United States has not a single synthetic nitrogen fertiliser works.

The yields of the Bradley-Lovejoy apparatus were rather good. They succeeded in converting as much as 2½ per cent of the air, which is somewhat better than their successors are able to accomplish.

But their units, 12 kilowatts, were very much smaller than the 1000 to 3000 kilowatts now used in Norway; they were also more delicate to handle, all of which made installation and operation considerably more expensive.

However, this was the natural phase through which any pioneer industrial development has to go, and it is more than probable that in the natural order of events, these imperfections would have been eliminated.

But the killing stroke came when financial support was suddenly withdrawn.

In the successful solution of similar industrial problems, the originators in Europe were not only backed by scientifically well-advised bankers, but they were helped to the rapid solution of all the side problems by a group of specially selected scientific collaborators, as well as by all the resourcefulness of well-established chemical enterprises.

That such conditions are possible in the United States has been demonstrated by the splendid team-work which led to the development of the modern Tungsten lamp in the research laboratories of the General Electric Company, and to the development of the Tesla polyphase motor by the group of engineers of the Westinghouse Company.

True, there are endless subjects of research and development which can be brought to success by the efforts of single independent inventors, but there are some problems of applied science which are so vast, so much surrounded with ramifying difficulties, that no one man, nor two men, however exceptional, can either furnish the brains or the money necessary for leading to success within a reasonable time. For such special problems, the rapid co-operation of numerous experts and the financial resources of large establishments are indispensable.

All these examples of the struggle for efficiency and improvement demonstrate why, in industrial chemistry, the question of *dollars and cents* has to be taken very much into consideration.

From this standpoint at least, the "Dollars and cents" argument can be interpreted as a symptom of industrial efficiency, and thus the definition sounds no longer as a reproach. With some allowable degree of accuracy, it formulates one of the economic aspects of any acceptable industrial chemical process.

Indeed, barring special conditions, as, for instance, incompetent or reckless management, unfair competition, monopolies, or other artificial privileges, the money success of a chemical process is the cash plebiscite of approval of the consumers. It is bound, after a time at least, to weed out the inefficient methods.

Some chemists, who have little or no experience with industrial enterprises, are too much over-inclined to judge a chemical process exclusively from the standpoint of the chemical reactions involved therein, without sufficient regard to engineering difficulties, financial requirements, labour problems, market and trade conditions, rapid development of the art involving frequent disturbing improvements in methods and expensive changes in equipment, advantages or disadvantages of the location of the plant, and other conditions so numerous and variable that many of them can hardly be foreseen even by men of experience.

And yet, these seemingly secondary considerations most of the time become the deciding factor of success or failure of an otherwise well-conceived chemical process.

The cost of transportation alone will frequently decide whether a certain chemical process is economically possible or not. For instance, the big Washoe Smelter, in Montana, wastes enough sulphur dioxide gas to make daily 1800 tons of sulphuric acid, but that smelter is too far distant from any possible market for such a quantity of otherwise valuable material.

Another example of the kind is found in the natural deposits of soda, or soda lakes, in California. One of these soda lakes contains from thirty to forty-two million tons of soda. Here is a natural source of supply which would be ample to satisfy the world's demand for many years to come. Similar deposits exist in other parts of the world, but the cost of transportation to a sufficiently large and profitable market is so exorbitant that, in the meantime, it is cheaper to erect at more convenient points expensive chemical works in which soda is made chemically and from where the market can be supplied more profitably.

In addition, we can cite the artificial nitrate processes in Norway, which, notwithstanding their low efficiency and expensive installation, can furnish nitrate in competition with the natural nitrate beds of Chile, because the latter are hampered by the cost of extraction from the soil where fuel for crystallisation is expensive, in addition to the considerable cost of freight.

But there is no better example, illustrating the far-reaching effect of seemingly secondary conditions upon

the success of a chemical process, than the history of the Leblanc soda process.

This famous process was the forerunner of chemical industry: for almost a century it dominated the enormous group of industries of heavy chemicals, so expressively called by the French, "La Grande Industrie Chimique," and now we are witnesses of the lingering death agonies of this chemical colossus. Through the Leblanc process, large fortunes have been made and lost; but even after its death, it will leave a treasure of information to science and chemical engineering, the value of which can hardly be overestimated.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, January 28, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

*"Influence of Salt-concentration on Hæmolysis."* By W. W. C. TOPLEY.

The method employed in this investigation has consisted in varying the percentage of sodium chloride present in a mixture of sheep's red cells, hæmolytic anti-body and complement. The hæmolytic anti-body was obtained from an immunised rabbit, and fresh guinea-pig serum, previously absorbed with sheep's red cells at 0° C., furnished the complement. Where hypotonic percentages of sodium chloride have been employed, the solutions have been made in 7·8 per cent saccharose solution.

The results have confirmed the observations of other workers that, when the percentage of salt is increased beyond the normal limit, hæmolysis is inhibited, owing to the failure of union between the complement and the red-cell anti-body complex, and that, if the amount of anti-body present in the mixture be increased, the effect of the increased salt concentration may to a certain extent be overcome.

It has further been shown that, if the salt concentration be decreased below the normal limits, less and less anti-body becomes necessary in order to bring about the union of red cells and complement, and that, in the almost entire absence of electrolytes, guinea-pigs' complement can hæmolyse sheep's red cells without the intervention of hæmolytic anti-body. This last fact had already been noted by others, but its significance had apparently not been realised.

It is possible that not the whole complement, but only some specialised part of it, causes this type of hæmolysis, but experiments in which the complementary serum was absorbed with sheep's red cells at 0° C. in a salt-free medium seemed to show that no anti-body of the usual type is involved.

*"The Life-cycle of Gladocera, with Remarks on the Physiology of Growth and Reproduction in Crustacea."* By G. SMITH.

*"Investigations on Protozoa in Relation to the Factor Limiting Bacterial Activity in Soil."* By T. GOODEY.

Two different lots of soil were taken and inoculated with cultures of protozoa originally obtained from soil, in order to determine whether the added protozoa would cause a decrease in the numbers of bacteria in the soil. One soil was free from protozoa to begin with, having been bottled since 1846, whilst the other was freed from protozoa by partial sterilisation. Separate lots of each soil were inoculated with cultures of ciliates, amœbæ, and flagellates, and suitable control samples were set up. Periodical bacterial counts were made, in order to ascertain if the protozoa were exerting a limiting action on

the soil bacteria, and these counts were continued over a period of about eighteen months.

The curves obtained on plotting the results of the bacterial counts indicate that in no case have the added protozoa brought down the numbers of bacteria to a lower level than the bacterial content of the soil samples containing no protozoa. It is further shown, in the case of one soil bottled in 1865, that, on moistening, the bacteria attain very high numbers in spite of the presence of a varied and numerically abundant fauna of amœbæ and flagellates.

The general conclusion drawn from the investigations is that ciliates, amœbæ, and flagellates do not act as the factor limiting bacterial activity in soil.

*"The Mesodermic Origin and the Fate of the so-called Mesoderm in Petromyzon."* By S. HATTA.

*"Influence of Homodromous and Heterodromous Electric Currents on Transmission of Excitation in Plant and Animal."* By Prof. J. C. BOSE.

## NOTICES OF BOOKS.

*The Chemistry of the Radio-elements.* By FREDERICK SODDY, F.R.S. Part I., Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1914.

THE new edition of this book has been practically rewritten, and is issued in two volumes, of which this, the first, deals more with practical knowledge than with theoretical generalisations. It opens with a lengthy and clear historical and descriptive account of the phenomena of radio-activity, explaining the meanings of such conceptions as the period of average life, the radio-active constants, and radio-active equilibrium. The work which has recently been done on the electro and colloidal chemistry of these elements is well described, and a general account is given of their chemical characters, with a short discussion of their position in the Periodic Table. Finally, the properties of the individual elements are described in turn in much detail, methods of estimation and separation being included. It is perhaps hardly necessary to say that the book is quite indispensable for the physicist or chemist who is interested in recent work on radio-activity.

*A Text-book of Practical Assaying.* By JAMES PARK. Revised and Enlarged from the Third New Zealand Edition. London: Charles Griffin and Co., Ltd. 1914.

THIS book contains a two years' course of assaying and technical analysis. The work is on the whole well graduated, although it would hardly seem advisable to defer all qualitative analysis to the end of the course. Technical methods of ore valuation are clearly described, and many fully worked examples are given, so that the student should have no difficulty in calculating his results. The analysis of coal, soils, manures, water, milk, &c., is included, and it seems quite probable that the book, which was originally written for New Zealand and Australian students, will be found useful in this country also.

*Aluminium Facts and Figures.* London: The British Aluminium Co., Ltd. 1914.

THIS pocket-book contains tables showing the physical properties of aluminium and data relating to wires, tubes, rods, circles, &c., made of the metal. Some of the different kinds of sections which the British Aluminium Company can supply are illustrated, and useful conversion and other tables are included. The pocket-book is conveniently issued in loose leaf form, and consists of several separate sections, each of which deals more particularly with the application of aluminium in one branch of industry.

## CORRESPONDENCE.

## ANILINE DYE SCHEME.

To the Editor of the Chemical News.

SIR,—I am being repeatedly asked for my views with regard to the Revised Government Scheme on National Dyes, and as to the criticism which has been directed against Professor Raphael Meldola's letter on the question of Science and Industry. I will deal with the Revised Government Scheme first.

It may be considered, as a scheme, slightly better than the first proposals put forward by the Government, but considered from the standpoint of the Chemical and Allied Industries as a whole, it is no better, but worse.

If the new Scheme is examined closely it will be seen that the Government are helping to create a monopoly on behalf of those Commercial Interests which are behind the Scheme, and who are anxious to obtain the Concession from the Government.

A subsidy of £100,000 is being given to the Company for research work, and the benefit of that work will obviously not be for the benefit of the Chemical and Allied Manufacturers who are not interested in the Scheme.

Broadly speaking a new Company is being brought into existence, concessions are being given to it, and a subsidy of £100,000, yet those Chemical and Allied Industries which have been struggling along for years with the adverse conditions which have existed in this country, and which are entitled to every consideration in the circumstances, are to be ignored. The public will, I am sure, realise the injustice of the proposals.

The second point to be dealt with is this, that the Committee who are dealing with this matter at the Board of Trade are a Committee of Users of Chemicals and not a Committee of Chemical Manufacturers. Users of Chemicals are no doubt in a position, from the experience they have gained, to judge what are good Chemicals, but that does not justify them in assuming that they know how to manufacture Chemicals as well as the man who has devoted his life to the subject.

To explain my point, a manufacturer of pumps cannot manufacture big guns and small arms. Whilst you may characterise both manufactures as being engineering propositions yet the technicalities involved absolutely prevents the pump maker making big guns and small arms, and *vice versa*. The whole essence of successful manufacture in any given industry is experience and knowledge.

Therefore, the proper course of procedure for the Government to follow is to consult with a Committee of Chemical Manufacturers and obtain their approval of any scheme which is put forward, and not endeavour to rush through a scheme which in all of its essentials is unsound and unfair to the Chemical Industry as a whole.

In an industry the successful development of which requires the highest scientific knowledge, the public must realise that the views expressed by Professor Raphael Meldola are absolutely sound. Certainly the views which he expressed in his admirable letter in *The Times* are those which the Germans rigidly adhere to, and is the secret of the considerable success which they have achieved in this sphere of activity.

In Germany there is the University trained Chemist for every fifteen men employed in the Chemical Industries, and the ratio covering all the industries in Germany is at the rate of one in forty.

These University trained Chemists are now, by the experience they have gained in industry, more efficient than the corresponding Chemists in England. The ratio of the University trained Chemist to labour in England is one in five hundred.

The point we now have to determine is as follows:—

Shall we concede to Chemical Users, who by their experience are not entitled to call themselves Chemical Manufacturers, the concession and subsidy which the

Government are prepared to offer, or shall we concede them to the Scientific Chemist and enable him to place himself on an equal footing with his German competitor?

Obviously the Scientific Chemist will become more efficient with the money so placed at his disposal in a shorter space of time than the Woollen Manufacturer who is a User of Chemicals.

The public must put a stop to the empirical methods which in the past have been characteristic of British industry; the situation is much too serious to allow them to proceed. Our happy-go-lucky methods, whilst they may have been successful in the past, will be disastrous for us if we continue them at the conclusion of the War.—I am, &c.,

(Signed) J. TAYLOR PEDDIE,  
Vice-President and Chairman.

Institute of Industry and Commerce,  
Aldwych Site, Strand, London, W.C.  
February 4, 1915.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 1, January 4, 1915.

**Determination of Saccharose in Beet Molasses. Method of Inversion by Double Neutral Polarisation.**—Emile Saillard.—When Clerget's method is used to analyse molasses the percentage of saccharose obtained is too low, owing chiefly to the presence of active nitrogenous substances. To eliminate the error, and also that due to the presence of certain salts which affect the rotatory power of saccharose, the author proposes a method of inversion by double neutral polarisation, the details of which are given in this paper. He determines the polarisations, before and after inversion, of the filtrate obtained from the molasses, and finds the coefficient of inversion by similar treatment of a solution of pure sugar of the same polarisation as the molasses solution.

## MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Royal Society of Arts, 8. (Fothergill Lecture). "Motor Fuel," by Prof. V. B. Lewis.
- TUESDAY, 16th.—Royal Institution, 3. "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S.
- WEDNESDAY, 17th.—Microscopical, 8. Presidential Address by Prof. G. Sims Woodhead, "Some of the Microbiological Problems of the Present War."
- Royal Society of Arts, 8. "The Decorative Textile Industries and the Designers' Relation thereto," by Arthur Wilcock.
- THURSDAY, 18th.—Royal Institution, 3. "Zoological Studies—War and Evolution, Nations as Species," by P. Chalmers Mitchell, F.R.S.
- Institute of Petroleum Technologists, 8. "The 'Cracking' of Oils, with a view to obtaining Motor Spirit and other Products," by W. A. Hall.
- Royal Society. "Gaseous Combustion at High Pressures," by W. A. Bone and others. "Orbits of a Charged Particle round an Electric and Magnetic Nucleus," by W. M. Hicks. "The Lunar Diurnal Magnetic Variation and its Change with Lunar Distance," by S. Chapman.
- Chemical, 8.30. "Dielectric Constants of some Organic Solvents at their Melting- or Boiling-points," by J. D. Canwood and W. K. S. Turner. "Preparation of Allyl Alcohol," by F. D. Chattaway. "Velocities of flame in Mixtures of Methane and Air," by A. Parker.
- FRIDAY, 19th.—Royal Institution, 9. "The Visit of the British Association to Australia," by Prof. H. E. Armstrong.
- SATURDAY, 20th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

**Liebig's Extract of Meat Company, Ltd.**—The directors have resolved to declare an interim dividend of 10 per cent, free of income tax, on the Ordinary shares of this company, being ten shillings per share, payable on and after February 15 next to the proprietors of Ordinary shares registered on the company's books on February 5 and to holders of Ordinary shares to bearer.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2882.

## SALTS COLOURED BY CATHODE RAYS AND THE MOLECULAR FORCE FIELD THEORY.

By Prof. E. C. C. BALY, F.R.S.

IN the CHEMICAL NEWS for January 15 a paper was published by Prof. Goldstein which he delivered before Section A of the British Association, and in which he gave an account of his most interesting results obtained by the action of cathode rays and of ultra-violet light upon metallic salts. Prof. Goldstein has shown that under the influence of either of these agencies coloured and metastable modifications of certain salts are formed which are characterised by new properties. Further, it appears that a pure salt does not behave in this way, but that the phenomenon is peculiar to solid solutions. He suggested the name of "distension" for this new condition of the salts. I have in several recent papers (Baly and Rice, *Chem. Soc. Trans.*, ci., 1475; ciii., 91, 2085; Baly and Krulla, *Ibid.*, ci., 1469; Baly, *Phil. Mag.*, xxvii., 632; *Zeit. Elektrochem.*, vii., 211; *Phys. Zeit.*, xiv., 893) developed a theory of chemical reactivity based on an extended series of observations of the absorption spectra of organic compounds, and it would seem that this theory is applicable to Prof. Goldstein's results, for such metastable conditions as described by him directly follow from this theory. Although the existence of these metastable phases has been proved in the case of many organic compounds, such had not been discovered in inorganic chemistry.

It follows from the Zeeman effect, and also from the phenomenon known as the pressure-shift of spectrum lines, that the atoms must possess electro-magnetic fields of their own. When two atoms, with their electro-magnetic fields differing in type, are brought together, there will tend to form an addition complex, due to the condensing together of the force lines of the two fields. Within this condensed field potential gradients will exist, and if these are sufficiently steep, one or more electrons will tend to move from one atom to the other. If this take place, a true chemical union between the two atoms will occur. Similarly, when two molecules, with force fields differing in type, are brought together, an addition complex will be formed, and, subject to the potential gradients being sufficiently steep, there will be a transference of electrons, with the result that new chemical individuals will be produced, and a chemical reaction will have taken place. If the gradients are insufficiently steep, the addition complex first formed will remain as such. There must exist, therefore, a complete gradation between the condition when a chemical reaction occurs and the condition when the two molecular fields, owing to their being alike, have no mutual influence. On these lines chemical reactivity is to be traced to the molecular fields, and primary valency in its stoichiometrical meaning is secondary, in the sense that it is a resultant effect following the formation of the addition complex.

If the general case of a molecular force field be considered, it is evident that if the component atomic fields happen to balance one another, the molecular field will entirely be closed. In such a case the molecule will have no reactivity, and no doubt this condition obtains in such compounds as HCl and NH<sub>3</sub>, which do not react when pure and dry. On the other hand, after the maximum possible condensation has taken place between the force lines of the component atomic fields, there may be left over an uncompensated balance. No doubt this condition is the origin of what is somewhat loosely called residual affinity. It follows from the foregoing that in order that a molecule with a closed field develop reactivity its closed field must be open or unlocked. The first method of opening the closed fields is by dissolving the compound

in a solvent possessing residual affinity. The free force lines of the solvent will interpenetrate the closed fields and open them, so that they can react with any other suitable substance dissolved in the same solvent. The condition, however, is a perfectly general one, for the closed fields may be opened when mixed with molecules possessing residual affinity, independently of whether an actual solution is formed or not. The second method of opening the closed fields is by the action of light. When the closed field molecules are mixed with other molecules possessing residual affinity, a type of equilibrium is set up between opened-up and non-opened-up molecules, and it is on this equilibrium that the reactivity of the system depends. Such a system can selectively absorb light, and the light in being absorbed shifts the equilibrium towards the reactive side—that is to say, it increases the relative number of opened up molecules present, a new photodynamic equilibrium being established.

Now, by a very simple application of the energy quantum theory, it can be shown that the opening-up process of any given force field must be discontinuous—that is, definite stages must occur, and when a force field is opened up it must exist in one or other of these stages. Each of these stages will be able to absorb definite light rays, and may at once be detected and differentiated by the frequencies of the absorption bands which they originate. Further, each of these stages must possess a specific chemical reactivity towards other compounds, and in order that a molecule can enter into a specific chemical reaction its force must be opened up to the required stage.

The above deductions follow simply enough from the general theory. The existence of these stages and their production can readily be shown by the various absorption bands exhibited by one and the same compound when dissolved in various solvents. It can also be shown that the opening up of a closed field to a definite stage is necessary before a specific reaction can take place. For example, when *p*-aminobenzaldehyde is dissolved in alcohol the solution shows a strong absorption band in the ultra-violet. There is, therefore, present one stage in the opening up of the closed field of the aldehyde formed by the residual affinity of the alcohol. If to this solution is added a little alcoholic HCl (about 0.2 eq.) a marked yellow colour is developed which disappears on further addition of the acid (Baly and Marsden (*Chem. Soc. Trans.*, xciii., 2108). The yellow colour is due to the presence of a new absorption band in the visible region, and when the further quantity of acid is added, the absorption spectrum changes to that of the hydrochloride of the base. Clearly therefore, there exists an intermediate stage in the reaction, in which the aminoaldehyde is converted into a reactive form, which proceeds, with more acid, to form the salt. This intermediate stage is the higher and more reactive stage in the opening up of the closed field, such as the theory prophesied. Such intermediate and highly opened-up stages have been found to exist in many reactions.

If the reverse process be considered—namely, the condensation of the atomic force lines to give the molecular field—it is evident that this process also must take place in stages. When any derivative is prepared, as it must indeed be prepared, from an opened-up stage of the parent compound, such derivative must at the moment of formation exist in the opened-up phase. There is no reason why, if suitable precautions are taken, such derivatives may not be maintained in this metastable and opened-up phase. Many such metastable substances have been obtained in recent years, as, for example, the highly-coloured, unstable forms of the nitrophenol ethers (Hantzsch and Gorke, *Ber.*, xxxix., 1073), of nitroanthrone (Hantzsch and Korczynski, *Ber.*, xlii., 1216), and many other compounds. All such compounds, as may be expected, are abnormally reactive, and change very readily into the ordinary stable forms. Up to the present the existence of this type of compound in a metastable condition, with its force field opened up to a relatively

high stage, has only been known in organic chemistry. Naturally they also should be able to exist in the case of inorganic salts, and Prof. Goldstein is the first to announce their discovery. Their instability and their abnormal selective absorptive power are the same properties as those possessed by their organic analogues. There seems no doubt that the condition named by Prof. Goldstein as one of distension is, indeed, the existence of the force fields of the salt in a higher stage of opening up than has hitherto been recognised. It has already been shown that the phenomena of the opening up of a given closed field are essentially connected with the presence of a solvent. This agrees entirely with Prof. Goldstein's observation that the formation of his highly coloured metastable forms of metallic salts is essentially a property of their solid solutions. A pure solid salt is not affected.

One point still remains to be considered. When any substance absorbs light, it is obvious that, provided no chemical change is produced, the whole of the absorbed energy must again be emitted. This emission must take place at some frequency which is a characteristic vibration of the absorbing system. In general this frequency lies in the infra-red region of the spectrum. Sometimes a portion of this energy is emitted in the visible region, when we have visible fluorescence or phosphorescence. In such cases, according to the energy quantum theory, the major portion of the energy escapes as fluorescent or phosphorescent emission, while the balance is still emitted as infra-red radiation. The difference between fluorescence and phosphorescence is merely a question of the velocity of the emission in relation to the velocity of absorption. If the former is much slower than the latter, the phenomenon is one of phosphorescence, and in certain cases the velocity of emission is so small that it is immeasurable. Such a condition involves the existence of the substance in one of the opened-up metastable stages with high energy content. The energy cannot escape, owing to the fact that the vibration frequencies at which it normally would be emitted are restrained. If, however, those vibrations are excited by the incidence of light of the same frequency, then the absorbed energy will at once escape. This phenomenon is well known, for if a potentially phosphorescent substance—that is to say, one in the metastable stage—is exposed to infra-red light the energy is rapidly emitted as phosphorescence, and the system returns to its normal stable condition. Exactly the same will occur if the metastable substance is exposed to light of the same frequency as the phosphorescent emission. It is only necessary by external means to excite the vibration at which the absorbed energy can escape for the mechanism to be set in action.

Prof. Goldstein has noted this phenomenon as being characteristic of his new forms of metallic salts, for they phosphoresce on exposure to daylight, and their colour begins to disappear. As shown previously, the highly coloured metastable salt is the normal salt with its force field opened up to a definite stage, such opening up being accompanied by an absorption of energy. The reverse process can only take place with evolution of this absorbed energy, an evolution which must occur at certain characteristic vibration frequencies. In general these vibrations are inactive, and so the emission of the energy is exceedingly slow, and the highly coloured salt remains in the metastable condition when kept in the dark. When, however, the new form is brought into the light the necessary vibrations are called into play, with the result that the previously absorbed energy is emitted and the salt phosphoresces and returns to the normal stable form.

Prof. Goldstein's new highly coloured salts conform, therefore, in every way to the deductions made from the force field theory, and it only remains for their abnormal reactivity to be proved. Whereas the existence of their analogues has clearly been established in organic chemistry, it is of great interest and importance that these unstable modifications have now been discovered among the inorganic metallic salts.

## THE SULPHATE IN RIVER WATERS.\*

(A REPLY).

By R. B. DOLE.

MR. H. S. SHELTON, in an article in *CHEMICAL NEWS* for Dec. 24, 1914 (vol. cx., p. 307), attempts to prove that the determinations of sulphate in river waters made by the United States Geological Survey in a long series of studies (see U.S. Geol. Survey Water-Supply Papers 236, 237, 239, 273, 274, 339, and 363) are grossly inaccurate and unreliable. I would not reply to his article if it were not for the fact that he misquotes the published account of the procedure used, and also casts suspicion not only on the reliability of all the water analyses made by the United States Geological Survey, but also on the reliability of all the rock analyses made by chemists of the world. Mr. Shelton's paper contains the following statements:—

"The method adopted by the analysts of the U.S.A. Geological Survey is described in detail. The principal difference between the method used and that described by me is that, before the analysis of the dissolved matter the filtered water is evaporated to dryness in a platinum vessel on a water-bath, and dried at 180° C. for one hour. Mr. Dole appears to think that the treatment is such as to negative my suggestion, and remarks that it 'precludes great error by retention of silicates or organic compounds in the precipitate.' . . . The suggestion that considerable error from retention of silicates or organic compounds is avoided by heating to 180° is highly disputable. I am, of course, aware that the silica in such a compound as sodium silicate is thrown into an insoluble form. Indeed, I am somewhat surprised that a portion of the aluminium is not thereby mixed with the silica. Mr. Dole, however, assumes too much if he states dogmatically that all silicon compounds are reduced to silica at that temperature, or that all organic compounds are decomposed. Indeed, both the latter statements are obviously wrong. That silicates or organic compounds, or both, cannot survive at 180°, and cannot afterwards be precipitated by an acid solution of barium chloride is a statement that requires definite experimental proof."

This quotation includes a misquotation of my outline of the procedure used in the laboratories of the United States Geological Survey and a series of misleading comments on the procedure. The procedure of which Mr. Shelton quoted only part is as follows (*CHEMICAL NEWS*, 1911, ciii., 289): "The filtered water was evaporated to dryness, invariably in platinum on a water-bath, and the residue was dried at 180° C. for one hour, being subsequently carbonised if much organic matter was present. The silica was then dehydrated by evaporation with hydrochloric acid, and filtered from the acid solution. Iron and aluminium were removed by precipitation with ammonium hydrate, after which the filtrate was slightly acidulated with hydrochloric acid, and was heated nearly to boiling. After excess of barium chloride in hot 10 per cent solution had been added, the liquid was digested on a hot plate for at least thirty minutes. The precipitate was removed by filtration, thoroughly washed with hot water, dried, ignited, and weighed. The amount of sulphates as parts per million of SO<sub>4</sub> was computed from that weight. This treatment certainly precludes great error by retention of silicates or organic compounds in the precipitate."

Any chemist will readily comprehend that this is essentially the general procedure the world over for determination of sulphate. The errors of the barium-chloride method of estimating sulphate have been investigated by Richards and Parker (*Proc. Am. Acad.*, 1896, xxxi., 67; *Zeit. Anorg. Chem.*, 1895, viii., 413), Hulett and Dushak (*Zeit. Anorg. Chem.*, 1904, xl., 196), Allen and Johnston (*Journ. Am. Chem. Soc.*, 1910, xxxii., 588; *Journ. Ind. and Eng. Chem.*, 1910, ii., 196), Hillebrand (*U.S. Geol. Survey, Bull.* 422, 1910), and many other competent

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chemists, none of whom has attributed to it the gross unreliability that Mr. Shelton insinuates. Indeed, the briefest review of the literature should convince the most captious critic that the barium-chloride method is the standard, accepted, widely-used method for determination of sulphate. The procedure outlined by me and quoted above provides for carbonisation of organic matter, removal of silica and silicates, and removal of iron and aluminium before precipitation with barium-chloride; consequently, Mr. Shelton's comments on his incomplete quotation of the procedure are irrelevant and inappropriate.

His assumption that all the evaporations were made on a water bath heated by the Bunsen is unfounded. The water-baths in the laboratories in which most of the analyses were made were heated by live steam from the boilers in the basement. Though Mr. Shelton's criticism is therefore not applicable to these analyses it may be added by way of comment that absorption of  $\text{SO}_2$  fumes could hardly be regarded as a serious source of error in determination of appreciable quantities of sulphate. Warington (*Journ. Chem. Soc.*, 1889, p. 545), to whom Mr. Shelton refers as authority, makes a passing comment on  $\text{SO}_2$  fumes in connection with determination of minute traces of sulphur in rain-water, but he gives no figures in support of his comment, and it is extremely doubtful that he would consider fumes from his gas-burners an appreciable source of error in determinations involving the weighing of 10 or 15 mg. of barium sulphate.

The purpose of this reply to Mr. Shelton's criticism has been to refute his charge that determinations of sulphate in water by chemists generally and by those of this Survey in particular are grossly inaccurate. It might be added by way of suggestion that Mr. Shelton investigate his alleged "discrepancy" by comparing the chemical composition of the river waters not only with the chemical composition of the crust of the earth but also with the composition of that part of the crust that is now subject to the disintegrating action of water, and further that he consider not alone the absolute quantities of the chemical constituents in the crust, but their relative solubility as well.

## THE LATER RESEARCHES ON ANTHOCYAN.

By P. Q. KEEGAN, LL.D.

IN 1911 V. Grafe and Combes expressed the opinion that there cannot exist a special chromogen of anthocyan, and this pigment is formed complete in all parts on the spot, and does not result from the simple oxidation of pre-existing substances. Combes states that in the leaf soluble sugary compounds accumulate in notable quantity, and thereby the process of oxidation becomes more active, and new phenolic compounds of a vivid red-violet or blue colour (anthocyanins) are now formed. I think that this sudden appearance of sugars or glucosides in the autumn leaf or petal is very doubtful, and even if it did happen it would not intensify the respiration one jot, and, moreover, there is stronger reason to conclude that the autumn erythrophyll does spring from a precursory chromogen than there is with regard to the chromogenic origin of the floral anthocyan. The old tinted leaf invariably contains uncoloured tannin, whereas in certain blue perianths tannin seems to be completely absent, the oxidation there being at times far more intense than it ever is in the leaf—intense enough apparently to completely destroy any tannoid or tannin that had ever been formed in the petals. The clearest indication that anthocyan is derived from a pre-existing chromogen seems to lie in the fact that in numerous cases the tannins of the plants by suitable treatment can be induced to assume a tint in solution which is absolutely comparable with that which the petals themselves exhibit in their natural condition; for

instance, the flowers of species of rhododendron, geranium, primula, rosa, and many others. There are cases, such as hyacinth, where the plant produces no tannin in any of its organs, but here again the floral pigment is strictly in accordance with the tannic chromogen that is produced by some of its congeners in their leaves or other parts. At all events there is conclusive evidence to prove that the protoplasm, however highly oxidised, which produces habitually and naturally a certain kind of tannin cannot and does not produce any or every kind of pigment in the corolla, and in this sense it may be held that there does decidedly exist a special chromogen of anthocyan; that is to say, in the formation of the original blue, certain aromatic nuclei are deassimilated which are not similar to those aromatic nuclei deassimilated in the formation of the original red. Moreover, according to some colour reactions, there exists in the deeper tinted petal less of the residuary tannic chromogen than in the paler petal, showing apparently that in the former case it has been nearly all utilised. In the deep tinted petal there is, as a rule, tannin and no flavone; in the pale petal there is flavone and no tannin; hence on an increased intensity of oxidation the tannin, being there, is at once oxidised to anthocyan, whereas if no tannin is present it would have to be first produced in limited quantity, and hence the total effect of the oxidation would be lessened, and a much paler tint would be the inevitable result. In some Leguminosae, however, where no tannin is formed, the avidity for nitrogen is so ardent that oxidation rises extremely high, and deep purples may be developed.

It has been stated by other authors that "chromogens of more than one kind exist in the different coloured varieties of stocks (*Matthiola*), or one chromogen is present associated with substances which determine the colour of the oxidised product of the chromogen." The varied colours are canary yellow, scarlet, blood-red, purple, azure-blue, &c. As no tannin is produced in the vegetative organs it follows that the chromogen of anthocyan is in this case organised in the floral parts alone; i.e., it is solely under the dominion of the organic requirements of neighbouring cells. It is not the associated substances which alone determine the depth or the character of the soluble pigments of the corolla, and there is only one chromogen so far as these are concerned. The variation in the colours depends entirely on the lesser or greater needs of the reproductive organs, and these needs seem in this genus to be impressed upon the seeds of the different varieties with a truly surprising constancy. It is very probable that the volatile oil present in the petals supplies by its oxidation the acid necessary to effect the change from blue to red. Another statement, that "as the water decreases in the petal cells the reducing agents of the cell become active and oxydase becomes inert," does not seem correct in view of the fact that after a spell of unusually dry and hot weather many white flowers, such as hawthorn, viburnum, deutzia, cow-parsnip, &c., assume a very pronounced red tint. This reddening effect may be due to the increased intensity of the sunlight, but light combats the turgescence of the epidermal cells of the corolla, and hence according to the quoted statement it ought to depress or destroy the oxydasic activity which is supposed to develop the red tint, the real cause of which is probably the removal of the air which in ordinary weather fills the intercellular spaces. I need not specially refer to Gautier's recent references to the specific pigments proper to each of the numerous races of the grape-vine, all of which pigments have a similar structure, viz., are feeble polybasic acids derived from the union to a trivalent radicle of three branches of polyphenol partly carboxylated (like aurine or fuchsine); nor to Willstätter's opinion (*Liebig's Ann.*, 1913) that the blue pigment of centaurea is a salt of a glucoside having three CO groups.

With regard to the chemistry of the chromogen, it is evident to me by the very tone and aspect of the soluble pigment produced that the precursor of the red must con-

tain many more reactive groups such as methylene  $\text{CH}_2$ , carbonyl  $\text{CO}$ , &c., than that of the blue. Strongly reactive phenols like phloroglucol, a conjugated or a "crossed system" of double linkings, or a condensation with elimination of oxygen, would obviously be fatal to the placidity and uniformity of a genuine cold and retiring blue. A chromophore either present or readily forthcoming, and an efficient number of auxochrome groups in proper positions would undoubtedly be indispensable. All these conditions, positive and negative, are fully satisfied apparently in the case of caffetannin. It behaves like a  $\beta$ -ketonic acid, it has no  $\text{CO}$  group or ethylene compound, has six  $\text{HO}$  groups, is not a glucoside, and is a kind of "lakey" combination of two molecules of caffeic acid with two molecules of quinic acid plus one molecule of water. Thus there are three hydroxyl groups in the ortho position and two in the para position relatively to one another; there is also a lateral group of three carbon atoms, viz.,  $\text{CH}=\text{CH}.\text{COOH}$ , showing a definite relationship to cinnamene,  $\text{C}_6\text{H}_5(\text{CH}=\text{CH}_2)$ . The quinic acid residue very readily yields a  $\text{CO}$  group, but there are only two other very reactive  $\text{CH}_2$  groups in the molecule of this tannin, so that altogether, while it is quite sufficiently though not extravagantly endowed with chromophoric groups, the presence of numerous and well placed auxochromes enables it to function as a very efficient chromogen of the softer and colder colorations. Its approach to cinnamene and to quinol, and its avoidance, as it were, of the highly reactive phloroglucol as a phenolic basis or nucleus, enable it on slight changes of its molecular structure to escape the grave disturbance and discoloration attendant on the formation of phlobaphene. In fact, to anyone sufficiently acquainted with the general reactions of the phloroglucol tannins as distinguished from those of caffetannin, it will appear perfectly evident that the chromogenic agency or activity of the latter must inevitably be of a much milder and "cooler" type than that of the former.

The views expressed in the preceding paragraph may seem to be based on some ill-digested theory or fanciful hypothetical assumption, but as a matter of fact they are absolutely not so in the slightest degree; they have really and naturally sprung up as the result of a studied contemplation of the facts. It was not long after a course of practical analysis of many common wild plants that it became increasingly evident to me that a true blue flower was invariably associated with a mildly reacting tannin which, on boiling with dilute mineral acid for a few minutes, gave no bright or muddy reddening of the liquid followed by a red-brown precipitate on cooling. At first I was misled by Stein's statement (1863) that "the blue pigment was none other than the saline (calcium) compound of the red matter, which appears to be paracarthamin," but I soon worked myself out of this fundamental error, and gradually grew convinced that it was only one kind of tannin that could possibly create an original true blue, and that this effect depended entirely on the constitution of the chromogen itself, and not at all on an incidental combination thereof with an alkali. Even in 1832 De Candolle stated that the red of hydrangea belongs certainly to blue; i.e., its chromule was less oxidised or more carbonated, while the red of rose belongs to the more oxidised (xanthic) series. He was, of course, not then aware of the grave differences as respects reactivity which the chromogens of the original pigments of these two flowers exhibit; but his statement nevertheless is highly significant, inasmuch as it demonstrates that even, thus early, observers were to be found who were acute enough to be able to detect the distinction between an original pigment and a non-original one.

Some of the later researches on anthocyan seem to be distinguished by a frantic attempt, begun in 1905 by Molisch, to obtain what was considered to be the pure pigment in a crystalline condition. Then also the highly confusing hypothetical subject of oxydases was introduced and brought to bear upon the origin of the floral colour or pigment. The result has been a tremendous amount of

work leading to little or no definite conclusion. A summary of my own conclusions may be condensed as follows:—

1. Plants producing phloroglucol tannins yield original reds only; plants producing caffetannin yield original blues only.
2. Plants producing gallotannin seem inclined (owing to less acid) to display vivid violets or warm purplish blues according to circumstances, but never cold true blues.
3. There is only one anthocyan pigment in plants producing caffetannin; the red on stem or petal is here due to acid only.
4. Yellow flowers are due to carotin or its diffused oxidised product (xanthophyll), and very rarely to a flavone.
5. The white flower very often encloses a very dilute solution of anthocyan, but is due chiefly to the circumstance that intense deassimilation has not been occasioned in the corolla, because the nitrogen needed by the reproductive organs has been fully supplied from sources other than the inflorescence.
6. Grate's opinion that "a special chromogen of anthocyan cannot exist" is incorrect so far as the specific hereditary tendency of the protoplasm to form certain kinds of tannin is concerned.

Patterdale, Westmoreland.

## STEEL INDUSTRY. OPPORTUNITIES FOR BRITAIN.\*

By WILLIAM LORIMER, LL.D.  
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THE war is affecting practically every industry in the country. In some cases its influence may be temporary, while in others it may be permanent. The purpose of this article is to inquire what is likely to be its effect—favourable or the reverse—on the steel trade of Great Britain, and whether it will provide an opportunity for regaining some of the markets which have been lost in recent years.

The output of the principal steelmaking countries of the world in 1913 was as follows, stated in millions of tons per annum—

United States .. ..	21 million tons.
Germany .. ..	15 million tons.
United Kingdom .. ..	7 million tons.
Russia .. ..	4 million tons.
Austria-Hungary .. ..	3½ million tons.
Belgium .. ..	2½ million tons.

Canada also is becoming a steel-producing country, and though its output is small in comparison with the above figures, it is increasing and will become important. A beginning has also been made with the production of steel in India and Australia, while one of the largest and most valuable deposits of iron ore in the world is now being worked in Newfoundland.

### Continental Production.

The two countries which have increased their production most rapidly during the past five years are Germany and Russia. In both there has been erected recently new plant which was not working up to its full capacity prior to the war. Germany's chief sources of ore supply are the Minette deposit in Lorraine and Luxembourg, east of the Moselle and north of Metz. This deposit is phosphoric, and consequently the great bulk of the German steel is basic.

In 1870 it was not known that this deposit was to any great extent workable beyond the boundaries of that portion of Lorraine which was annexed by Germany. It is

\* Read at the Institute of Industry and Commerce. From the *Glasgow Herald*.

now known that French Lorraine contains a larger quantity of rather better quality than German Lorraine, the approximate figures being—

French Lorraine ..	3000 million tons.
German Lorraine ..	1800 million tons.
Luxemburg .. ..	250 million tons.

The discovery in 1877 of the basic process of steelmaking gave an immense impetus to the development of this deposit, and the output of German Lorraine rose from about one million tons in 1880 to about 30 million tons in 1913. The development of the deposit in French Lorraine has been very rapid recently, and the output in 1913 was about 15 million tons, large quantities of which were exported to Germany and Belgium. Germany also imports about 10 million tons of ore from other sources, chiefly cheap qualities of phosphoric hematite. It will be seen from this that should Germany, as a result of the war, be compelled to surrender Lorraine to France her sources of ore supply will be seriously affected, and the cost of her purchases will, in all probability, be considerably increased. At present the whole area of the Minette deposit is within the German lines.

Germany has also large reserves of coal, which have been rapidly developed during recent years, and in many cases the steel companies own their own collieries. They have also developed in a marked degree the system of utilising the waste gases from coke ovens and blast furnaces in the process of steel manufacture, and by this means they have reduced the consumption of coal per ton of steel to a minimum.

The United States have enormous supplies of cheap fuel, and also large supplies of fairly high-grade ores, which, although seldom found in proximity to the steel works, are developed on a very large scale with special arrangements for economical transport, so that as yet comparatively small quantities of ores have been imported. About one-half of the steel produced in the States is acid and one-half basic.

The increase in the production of steel in the United Kingdom in recent years has been relatively insignificant as compared with the United States or Germany. In steelmaking, as in so many other industries, Great Britain has been a pioneer. We began years before the basic system was invented, and thus have relatively a much larger proportion of our plant devoted to the manufacture of the purer and costlier acid steel than any other country in the world.

#### *Supplies of Ore.*

Our output of acid steel has remained practically stationary for the last ten years, being round about four million tons per annum, while our output of basic steel has increased from one million to about three million tons. The primary reason for the absence of growth in the production of acid steel is the difficulty of getting, at a low enough price, increased quantities of the pure ores practically free from phosphorus which are necessary for its manufacture. On the other hand, deposits of phosphoric ore are found in all parts of the world, and as many of them are of vast extent, they can be worked cheaply, so that basic steel can be produced at a considerably lower cost than acid steel.

In the United Kingdom there are large reserves of low-grade phosphoric ores containing less iron than the Minette deposits of Lorraine, but they are somewhat scattered and are not always near the coalfields or near existing steel works.

There are also large reserves of coal, but the cost of production of coal, as will be noticed later, has risen very seriously in recent years, and as many of the companies producing steel are comparatively small, and have to buy their pig-iron and coal, it has not been possible to utilise waste gas to the same extent as in Germany. Then the wages paid to certain groups of workmen are very high, and no adequate allowance has been made, in fixing

wages, for increased facilities for cheapening production. These factors, combined with the National Insurance Act, the Mines Regulation Acts, and similar legislation have so enhanced the cost of production that foreign competition has become increasingly difficult to meet.

In Russia there are large quantities of both ore and coal, and the principal development has been near the Black Sea. The home market is highly protected, and as yet comparatively small quantities have been available for export.

France, while rich in iron ore, is comparatively poor in reserves of coal. During the past five years there have been considerable developments of iron ore mines in the West of France, partly controlled by German firms, while quite recently French firms have acquired large interests in the newly discovered coalfield in Kent.

Austria-Hungary is relatively poor in both iron ore and coal reserves, nevertheless a considerable amount of modern steel plant is operated.

Belgium has not much coal and very little ore, but considerable supplies are drawn from Luxemburg, just across the border, and there are extensive modern works near Liège. There are considerable deposits of ore in the Belgian colony in the Congo, but the operation of these will probably belong to the time when we shall have to draw our supplies from the Southern Hemisphere.

#### *Germany Preparing.*

At the outbreak of the war the steel trade was nowhere good, but it was better in Germany than in Great Britain. Various causes had been in operation to produce this result. As we know now long preparation has been made for "The Day," and this involved the manufacture of enormous quantities of war material for use by land and sea. Germany's home market is secured to its manufacturers by high protective duties. It is of course a truism to say that a maximum output can be produced at a much cheaper rate per ton than a minimum, and the application of this principle, combined with remunerative prices obtained for work for the home market, has enabled the German manufacturers to make a fairly successful effort to capture our export trade and to obtain a footing in our home markets.

This effort has been carefully and systematically organised by a syndicate of manufacturers, who, no doubt, allot the foreign orders to the works best suited to execute them at the lowest cost. This can be done much more easily than would be possible in Great Britain in existing conditions, for an outstanding feature of the German steel industry is that it is controlled by a very few large companies. Incidentally it may be remarked that anti-trust legislation has probably checked to some extent similar methods of combined action in the United States. For some years prior to the war the available plant in that country was not working up to its capacity, and the increase in production has not been relatively as large as that of Germany.

Immediately before the outbreak of the war the steel trade of Great Britain was in a very unsatisfactory condition. At the beginning of 1912 activity in the shipbuilding and other trades had created a good demand for steel in all parts of Europe. Unfortunately for us it happened that coincidentally with this occurred the national coal strike, which stopped production for two months, and had very far-reaching effects. When the coal strike was settled great pressure was put on the steel work for deliveries, and while arrears were being worked off prices were maintained at a high level. At the same time, however, the pressure for deliveries on German works was never so great, and quite a number of new plants were put to work. The result of these conditions was that large quantities of German material were contracted for by British consumers of steel, and by the middle of 1913 British mills were short of orders and could only be kept going on a very much reduced output.

*British Difficulties.*

The increased purchases from Germany at this time were perhaps, in the circumstances, inevitable, but probably few realise how unfavourably our position in international competition has been affected by this strike and by the legislation already referred to. The most serious feature of our present position is the increased cost of production. To take one item only. If we compare the year 1904 with the spring of 1914 it will be found that for the manufacture of one ton of acid steel plates made in Scotland from ores imported from abroad the cost of the coal used has been increased by no less than 14s. 6d. per ton of plates. This result has been arrived at in spite of improvements in plant reducing the consumption of coal, and as a matter of fact the small output during the spring of 1914 just about neutralised the effect of the improvements.

Immediately on the declaration of war not only was there an instant cessation of imports of German steel into this country, but German exports to neutral markets were also stopped by the closing of German ports. As our own ports were open and the seas practically clear it looked as if the world's business in steel might be shared by ourselves and the United States, but it quickly became evident that there was no export business for either country. The magnitude of the struggle and of the interests involved so dislocated international finance that international business was paralysed, and therefore while there was great activity in the production of war material, exports of steel of the ordinary kind were almost entirely suspended. The financial arrangements of the Government have, however, proved very effective, and within the past few weeks there has been a greatly improved demand for steel for export, while the numerous shipbuilding orders recently placed have increased the demand for home consumption.

The Commercial Intelligence Department of the Board of Trade have issued a series of memoranda showing the extent of German trade in neutral markets and the openings they afford for British manufacturers, and it is to be hoped that they will receive the full and careful study which they deserve. Even in respect of the steel trade alone the details are too numerous to permit of their being embodied in this article, but one or two figures may be given.

The value of iron and steel plates and sheets exported by Germany in 1912 was £3,523,000, of which over half a million was imported into the United Kingdom, about half as much was sent to India and the Dominions, and the rest to neutral markets. British exports in the year 1913 amounted to £2,813,000.

Germany's exports of rails in 1912 amounted in value to £2,900,600, of which £129,900 represented imports into the United Kingdom, and £205,300 into India and the Dominions. British exports in 1913 amounted to £3,457,800. Of railway wheels and axles complete and tyres and axles loose Germany exported in 1912 £1,377,000, of which the United Kingdom took £40,000 and India and the Dominions £349,000. For the year 1913 British exports amounted to £1,210,000, of which India and the Dominions took £783,000.

*British Opportunities.*

These are only a few of the figures which might be enumerated, and it is obvious that they indicate a most valuable opportunity for largely increasing our export trade. Some of the countries referred to as neutral markets are no longer neutral, for they include our Allies—France, Russia, Belgium, and Japan—and they also include such friendly countries as Italy and Roumania, who must resent, and will continue to resent, the economic pressure to which German policy has subjected them.

Such trade as these countries can meanwhile afford must almost of necessity come to us, but we ought to make it our business to retain it in the future. How is

this to be done? One thing we ought emphatically not to depend on is sentiment. No doubt it will help us for a time, but it would be weakness and folly to trust to it permanently.

The Government of the Commonwealth has forbidden Government purchases from Germany in the future, and that is probably indicative of the feeling that will prevail among our Dominions and Dependencies. But we have to think of the ordinary consumer, who is an important factor in the maintenance of this industry. At present he is a sincere and full-hearted patriot, but "when the hurly-burly's done, when the battle's lost and won," and he settles down to the old conditions of peaceful trading, it will be in no way surprising if his love for the cheapest market so revives that if patriotic sentiment were put in one scale and half-a-crown a ton in the other the former would kick the beam.

In considering, then, what is to be done let it be clearly understood that nothing is imported into this country which cannot be equally well made here, and that every neutral market in the world is open to us at a price. The one essential factor in the extension and retention of our trade is a reduction of costs, both in production and in distribution. With respect to the latter the German system is one of combination as against our system of individualism, and it has certainly produced striking results. It will be well worth while for our own manufacturers to consider the feasibility of a closer alliance of the present producing companies, so that orders for all classes of steel may be executed at the mills best suited for the various products. Such an alliance would facilitate the creation of a better selling organisation, and it should keep its members in close touch with the official British Trade Commissioners settled in all parts of the world, who are eager to help British manufacturers and who are constantly rendering valuable assistance to all who apply for it.

With respect to reduced cost of production, while, as already indicated, the conditions at home are not so favourable as in Germany for the utilisation of waste gas, still, wherever this and the utilisation of exhaust steam are possible, the subject should have the most careful consideration.

*Attitude of Trade Unions.*

With regard to wages, manufacturers have not been quite fairly treated by the trade unions. When the making of open-hearth steel began a 25-ton furnace was a large one, and the wage rate per ton was fixed on this basis. Now furnaces of 60 tons capacity are quite common, but the rate per ton remains the same. But wages are either high or low only relatively to production. American wages are the highest in the world, but they are really lower than ours in relation to the output of the mills and furnaces. A sustained maximum output will reduce costs, will provide high wages, and will ensure employment; for only through full economic production can demand be regularly maintained. Restriction of output is unsound in principle and mischievous in its effect on employer and workman alike.

There are large markets open to us in Norway, Sweden, the Netherlands, and Switzerland. Hitherto these have been almost monopolised by Germany. In Russia, Italy, Japan, and our own Dominions Germany's predominance is much less marked, but it has nevertheless a very considerable share of the trade which the sympathetic feeling of the allied and friendly countries should make it easy for us to capture, if sufficient energy is displayed and if reasonable prices are quoted. A manufacturer will naturally and properly seek to obtain a reasonable profit on his costs, but these should be costs determined not by the use of obsolete plant but of an equipment designed and intended to produce the most economical results, so that if present exigencies give him admission into new markets he may in the future be able to retain them on his merits.

*Defective Business Methods.*

During the past two years I have been in many parts of the world and have heard complaints of our business methods constantly repeated. These may be stated here, though they are not applied exclusively, or even specially, to the steel trade. For instance, Colonial and foreign buyers complain that the British manufacturer will not supply what they want, but what he thinks they should use, because it is what he is in the habit of making. He would do better to act on the principle that it is his business to supply as cheaply as possible what the world's markets require, not something else and not necessarily something better.

Then, again, if a man wants to buy at a price per kilo instead of per ton, why put any difficulty in his way? Nothing more is involved than a simple calculation. Or if he wishes to pay in francs, in roubles, or in dollars, why not? It is simply a question of exchange. His catalogues and price lists ought to be prepared in the language of the country to which they are to be sent, and while currency varies nearly everywhere he should be prepared whenever necessary to express his measurements in metrical dimensions. The point is that we ought to adapt ourselves to the buyer's conditions and make it easy and not difficult for him to do business with us.

Preparation should be made not only for an early future but for a future more remote. As it was in 1870 and afterwards so it is likely to be again. When the war ends there will be much wastage which will have to be replaced in our Navy and in our mercantile marine, although if the German Fleet is handed over to us as part of our indemnity the expenditure necessary on our Navy will be materially reduced. But all this frightful expenditure by the nations involved, in men and in money—an expenditure which is producing no economic return—will impoverish the world for years. Remunerative expenditure and all expenditure not imperative must be curtailed until the capital destroyed is, at least in part, replaced, and therefore while we may expect a great outburst of trade at the close of the war, it will probably be followed by a period of restricted demand and keen competition. Let this be kept well in view in all preparation for the future.

I am much indebted to my friend and colleague, Mr. Wallace Thorneycroft, for the trouble he has taken in collecting for me the statistical information contained in this article.

ON THE ACTION OF LEAD, COPPER, TIN, NICKEL, ZINC, AND ALUMINIUM ON WATER.

By Dr. W. P. JORISSEN, The University, Leiden, Holland.  
(Continued from p. 80).

13. Lead.

ABOUT the corrosion of lead the same introductory remarks may be made as in the case of tin. The electrochemical potential is 0.151 volt, the overvoltage according to Caspario 0.64 volt, according to Mott 0.50 volt. Consequently a liberation of hydrogen from dilute sulphuric acid and other acids is not to be expected. However, in the presence of air oxidation of hydrogen on the surface of the metal takes place, the catalytic influence of the metal being considerable (Note 85).

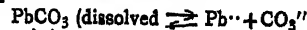
The action between lead and water containing air has been studied extensively (Note 86). Th. Paul, W. Ohlmüller, R. Heise, and Fr. Auerbach (Note 87) especially have chosen a more systematic way of trying to solve the problem than their predecessors. Their experiments have been continued by M. Pleissner (Note 88). He observed that water wholly free from carbonic acid but containing much solved oxygen generated at first a brown film, then a greenish yellow powder, PbO (solubility at 18° 0.31 millimol. Pb per litre = 64 mgrms. Pb = 69 mgrms. PbO).

In water, containing air free from carbonic acid, a white hydrate, (PbO)<sub>2</sub>.H<sub>2</sub>O (solubility at 18° 0.45 millimol. Pb per litre = 93 mgrms. Pb = about 100 mgrms. PbO), and perhaps other hydrates are formed.

The presence of carbonic acid considerably lowers the percentage of dissolved lead according to the experiments of Paul, Ohlmüller, Heise, and Auerbach. For instance, when the water contained about 40 mgrms. carbon dioxide and about 8 mgrms. oxygen per litre, only about 10 mgrms. Pb per litre were found, a basic carbonate being probably formed (the solubility of the normal carbonate is 0.002 millimol. = 0.04 mgrm. Pb per litre).

When sodium hydrocarbonate is added, the quantity of dissolved lead is still further reduced. In a solution of 8–9 mgrms. oxygen and 35 mgrms. NaHCO<sub>3</sub> per litre only 0.6 mgrm. Pb per litre was found (at 18°). Carbonic acid causes this quantity to increase. In water containing per litre 8.3 mgrms. oxygen, 35.3 mgrms. NaHCO<sub>3</sub>, and 32–33.4 mgrms. CO<sub>2</sub>, about 1 mgrm. Pb (at 18°) appeared to be present.

Suppose—for simplicity's sake—the solution to be saturated with PbCO<sub>3</sub> (Note 89). Then we have the equilibrium—



Consequently,  $(\text{Pb}^{++}) \cdot (\text{CO}_3^{--}) = k \cdot (\text{PbCO}_3)$ , or, as  $(\text{PbCO}_3)$  is constant,  $(\text{Pb}^{++}) \cdot (\text{CO}_3^{--}) = \text{constant}$  (solubility product, as a rule, represented by  $L$ ).

From  $(\text{Pb}^{++}) = \frac{L}{(\text{CO}_3^{--})}$  it follows that the quantity of lead dissolved in the water will decrease when Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> is added.

If carbonic acid is also present, we have to take into consideration the equation—

$$(\text{CO}_3^{--}) = \frac{k_2}{k_1} \cdot \frac{(\text{HCO}_3^-)^2}{(\text{H}_2\text{CO}_3)} \quad (\text{see p. 68}).$$

Consequently,—

$$(\text{Pb}^{++}) = \frac{L \cdot k_1}{k_2} \cdot \frac{(\text{H}_2\text{CO}_3)}{(\text{HCO}_3^-)^2},$$

meaning that the quantity of lead in the solution will be increased by adding carbonic acid and diminished if hydrocarbonate be added.

As lead sulphate is much more soluble than lead carbonate (solubility at 18° 0.126 millimol. PbSO<sub>4</sub> per litre = 38 mgrms. PbSO<sub>4</sub> = 26 mgrms. Pb) Paul, Ohlmüller, Heise, and Auerbach also investigated the influence of sodium sulphate. When at a temperature of 18° about 8.5 mgrms. oxygen, 35.5 mgrms. NaHCO<sub>3</sub>, 71 mgrms. Na<sub>2</sub>SO<sub>4</sub>, and 33.8–34.7 mgrms. CO<sub>2</sub> were present per litre, a quantity of about 3 mgrms. lead was found per litre.

Although the quantity of Pb-ions cannot be increased by adding Na<sub>2</sub>SO<sub>4</sub> or PbSO<sub>4</sub>, as it only depends on the least soluble lead salt (viz., PbCO<sub>3</sub>), the total quantity of dissolved lead increases in consequence of dissolving PbSO<sub>4</sub> molecules.

As lead chloride is again much more soluble than lead sulphate (solubility at 18° 33.6 millimol. per litre = 9.34 grms. PbCl<sub>2</sub> = 6.955 mgrms. Pb) the total quantity of dissolved lead will increase if a chloride be added.

In the extensive literature mentioned in the publications referred to in Note 86 many observations are to be found about the influence of dissolved substances in water containing air (drinking water, &c.) on the corrosion of lead. But the results often seem to contradict one another. Although a systematic investigation on the influence of all the substances found in varying quantities in different waters would of course add much to our knowledge of the solubility of lead in these waters, it would not be easy to predict from the analysis of some water or other its conduct towards lead. In practice it will be much easier and more reliable to make an accurate experiment with the water in question. Only then will it be possible to fully



imitate the circumstances under which the said water will come in contact with the lead to be used, pure or not (Note 90).

It may be remarked that in the experiments of Paul, Ohlmüller, Heise, and Auerbach and those of Fleissner stress is laid principally on the quantity of the lead compounds which dissolve in the water which is brought in contact with the lead. About the rate of oxidation of lead in contact with salt solutions of different composition and its dependence on this composition very little is known. This is also the case with the circumstances under which a protective layer is sometimes formed on the lead and its dependence on the composition of the water. Perhaps in this process some part is played by passivity.

According to Galdensteen Egeling and M. Müller (Notes 91 and 92) only the hydrocarbonates are able to generate a protective layer; others, for instance, Kühnemann (Note 93), are of opinion that sulphates also act in this way (Note 94).

#### Notes.

85. Sackur, *Arb. Kais. Gesundh.*, amte xxii., 205, 1905. See for the formation of hydrogen peroxide during the oxidation of lead amalgam in the presence of dilute sulphuric acid, F. Schönbein, *Fourn. Prakt. Chem.*, 1864, xciii., 25.

86. See the literature mentioned by G. Wolfhügel, *Arb. Kais. Gesundh.*, amte ii., 146, 484, and by Kühnemann, *Viertelj. schr. f. ger. Med. u. öffentl. Sanitätsw.*, 1904, xxvii., 314; also Woudstra and Snuif, *Chem. Weekbl.*, 1912, 447, 1013; Meerburg, *Ibid.*, 1912, 494.

87. *Arb. Kais. Gesundh.*, amte xxiii., 333, 1906, also published separately.

88. *Ibid.*, 1907, xxvi., Heft iii., also published separately, "Ueber die Löslichkeit einiger Bleiverbindungen in Wasser."

89. When a basic carbonate is present instead of this normal carbonate, the reasoning is the same; in which case, of course, the concentration of the OH-ions also figures in the solubility product, and there will be the fewer Pb-ions, in proportion as the concentration of the OH-ions will be more considerable.

90. Vide also the communications by J. W. de Waal, *Chem. Weekbl.*, 1909, vi., 987, who also mentions my advice. About an accelerating influence of the presence of some tin, see *Ibid.*, 1912, 454. For the manufacture of the so-called composition pipes as a rule very impure lead is used. Both the outside and the inside of the pipe are coated with a film of tin.

91. *Pharm. Weekbl.*, 1904, 561.

92. *Fourn. Prakt. Chem.*, 1887, xxxvi., 317.

93. *Viertelj. schr. f. ger. Med. n. öffentl. Sanitätsw.*, 1904, xxvii., 314.

94. Compare the above mentioned solubilities of lead carbonate and lead sulphate.

(To be continued).

## SOME ASPECTS OF INDUSTRIAL CHEMISTRY.\*

By L. H. BAEKELAND, Sc.D.

(Continued from p. 83).

HERE, then, is a very well worked-out process, admirably studied in all its details, which, in its heroic struggle for existence, has drawn upon every conceivable resource of ingenuity furnished by the most learned chemists and the most skilful engineers, who succeeded in bringing it to an extraordinary degree of perfection, and which, nevertheless, has to succumb before inexorable, although seemingly secondary, conditions.

Strange to say, its competitor, the Solvay process, entered into the arena after a succession of failures. When Solvay, as a young man, took up this process, he was,

himself, totally ignorant of the fact that no less than about a dozen able chemists had invented and reinvented the very reaction on which he had pinned his faith; that, furthermore, some had tried it on a commercial scale, and had, in every instance, encountered failure. At that time, all this must, undoubtedly, have been to young Solvay a revelation sufficient to dishearten almost anybody. But he had one predominant thought to which he clung as a last hope of success, and which would probably have escaped most chemists; he reasoned that, in this process, he starts from two watery solutions, which, when brought together, precipitate a dry product, bicarbonate of soda; in the Leblanc process, the raw materials must be melted together, with the use of expensive fuel, after which the mass is dissolved in water, losing all these valuable heat units, while more heat has again to be applied to evaporate to dryness.

After all, most of the weakness of the Leblanc process resides in the greater consumption of fuel. But the cost of fuel, here again, is determined by freight rates. This is so true that we find that the last few Leblanc works which manage to keep alive are exactly those which are situated near unusually favourable shipping points, where they can obtain cheap fuel, as well as cheap raw materials, and whence they can most advantageously reach certain profitable markets.

But another tremendous handicap of the Leblanc process is that it gives as one of its by-products, hydrochloric acid. Profitable use for this acid, as such, can be found only to a limited extent. It is true that hydrochloric acid could be used in much larger quantities for many purposes where sulphuric acid is used now, but it has, against sulphuric acid, a great freight disadvantage. In its commercially available condition, it is an aqueous solution, containing only about one third of real acid, so that the transportation of one ton of acid practically involves the extra cost of freight of about two tons of water. Furthermore, the transportation of hydrochloric acid in anything but glass carboys involves very difficult problems in itself, so that the market for hydrochloric acid remains always within a relatively small zone from its point of production. However, for a while at least, an outlet for this hydrochloric acid was found by converting it into a dry material which can easily be transported; namely, chloride of lime or bleaching-powder.

The amount of bleaching-powder consumed in the world practically dictated the limited extent to which the Leblanc process could be profitably worked in competition with the Solvay process. But even this outlet has been blocked during these later years by the advent of the electrolytic alkali processes, which have sprung up successfully in several countries, and which give as a cheap by-product, chlorine, which is directly converted into chloride of lime.

To-day, any process which involves the production of large quantities of hydrochloric acid, beyond what the market can absorb as such, or as derivatives thereof, becomes a positive detriment, and foretells failure of the process. Even if we could afford to lose all the acid, the disposal of large quantities thereof conflicts immediately with laws and ordinances relative to the pollution of the atmosphere or streams, or the rights of neighbours, and occasions expensive damage suits.

Whatever is said about hydrochloric acid, applies to some extent to chlorine, produced in the electrolytic manufacture of caustic soda. Here again the development of the latter industry is limited, primarily, by the amount of chlorine which the market, as such, or as chlorinated products, can absorb.

At any rate chlorine can be produced so much cheaper by electrolytic caustic alkali processes than formerly, and in the meantime the market price of chloride of lime has already been cut about in half.

In as far as the rather young electrolytic alkali industry has taken a considerable development in the United States, let us examine it somewhat nearer—

\* The Chandler Lecture, Columbia U S A., 1914.

At present the world's production of chloride of lime approximates about half a million tons.

We used to import all our chloride of lime from Europe, until about fifteen years ago, when the first successful electrolytic alkali works were started at Niagara Falls. That ingenious mercury cell of Hamilton Y. Castner—a pupil of Professor Chandler and one of the illustrious sons of the Columbia School of Mines—was first used, and his process still furnishes a large part of all the electrolytic caustic soda and chlorine manufactured here and abroad.

At present about 30,000 electrical horse-power are employed uninterruptedly for the different processes used in the United States, and our home production has increased to the point where, instead of importing chloride of lime, we shall soon be compelled to export our surplus production.

It looks now as if, for the moment at least, any sudden considerable increase in the production of chloride of lime would lead to over-production until new channels of consumption of chloride of lime or other chlorine products can be found.

However, new uses for chlorine are being found every day. The very fact that commercial hydrochloric acid of exceptional purity is now being manufactured in Niagara Falls by starting from chlorine, indicates clearly that conditions are being reversed; no longer than a few years ago, when chlorine was manufactured exclusively by means of hydrochloric acid, this would have sounded like a paradox.

The consumption of chlorine for the preparation of organic chlorination products utilised in the dye-stuff industry is also increasing continually, and its use for the manufacture of tetrachloride of carbon and so-called acetylene chlorination products has reached quite some importance.

There is probably a much overlooked but wider opening for chlorinated solvents in the fact that ethylene-gas can be prepared now at considerably lower cost than acetylene, and that ethylene-chloride, or the old known "Dutch Liquid," is an unusually good solvent. It has, furthermore, the great advantage that its specific gravity is not too high, and its boiling-point, too, is about the right temperature. It ought to be possible to make it at such a low price that it would find endless applications where the use of other chlorination solvents has thus far been impossible.

The chlorination of ores for certain metallurgical processes may eventually open a still larger field of consumption for chlorine.

In the meantime, liquefied chlorine gas, obtained by great compression, or by intense refrigeration, has become an important article of commerce, which can be transported in strong steel cylinders. Its main utilisation resides in the manufacture of tin chloride by the Goldschmidt process for reclaiming tin-scraps. It is finding, also, increased applications as a bleaching agent and for the purification of drinking water, as well as for the manufacture of various chlorination products.

Its great handicap for rapid introduction is again the question of freight, where heavy and expensive containers become indispensable.

In most cases the transportation problem of chlorine is solved more economically by handling it as chloride of lime, which, after all, represents chlorine or oxygen in solid form, easily transportable.

It would seem as if the freight difficulty could easily be eliminated by producing the chlorine right at the spot of consumption. But this is not always so simple as it may appear. To begin with the cost of an efficient plant for any electrolytic operation is always unusually high as compared to other chemical equipments. Then, also, small electrolytic alkali plants are not profitable to operate. Furthermore, the conditions for producing cheap chlorine depend on many different factors, which all have to co-ordinate advantageously; for instance, cheap power, cheap fuel, and cheap raw materials are essential, while,

at the same time, a profitable outlet must be found for the caustic soda.

Lately there has been a considerable reduction of the market price of caustic soda; all this may have for effect that the less efficient electrolytic processes will gradually be eliminated; although this may not necessarily be the case for smaller plants which do not compete in the open market, but consume their own output for some special purpose.

Several distinct types of electrolytic cells are now in successful use, but experience seems to demonstrate that the so-called diaphragm cells are cheapest to construct and to operate, provided, however, no exception be taken to the fact that the caustic soda obtained from diaphragm cells always contains some sodium chloride, usually varying from 2 to 3 per cent, which it is not practical to eliminate, but which, for almost all purposes, does not interfere in the least with its commercial use.

Mercury cells give a much purer caustic soda, and this may, in some cases, compensate for their more expensive equipment and operation. Moreover, there are some purposes where the initial caustic solution of rather high concentration, produced directly in these cells, can be used as it is without further treatment, thus obviating further concentration and cost of fuel.

The expenses for evaporation and elimination of salt from the raw caustic solutions increase to an exaggerated extent with some types of diaphragm cells, which produce only very weak caustic liquors. This is also the case with the so-called "gravity cell," sometimes called the "bell type," or "Aussig type," of cell. But these gravity cells have the merit of dispensing with the delicate and expensive problem of diaphragms. On the other hand, their units are very small, and, on this account, they necessitate a rather complicated installation, occupying an unusually large floor space and expensive buildings.

The general tendency is now towards cells which can be used in very large units, which can be housed economically, and of which the general cost of maintenance and renewal is small; some of the modern types of diaphragm cells are now successfully operating with 3000 to 5000 ampères per cell.

As to the possible future improvements in electrolytic alkali cells, we should mention that in some types the current efficiencies have practically reached their maximum, and average ampère efficiencies as high as 95 to 97 per cent have been obtained in continuous practice. The main difficulty is to reinforce these favourable results by the use of lower voltage, without making the units unnecessarily bulky, or expensive in construction, or in maintenance, all factors which soon outweigh any intended saving of electric current.

Here, more than in any other branch of chemical engineering, it is easy enough to determine how "good" a cell is on a limited trial, but it takes expensive, long continuous use on a full commercial scale, running uninterruptedly day and night for years, to find out how "bad" it is for real commercial practice.

In relation to the electrolytic alkali industry, a great mistake is frequently committed by considering the question of power as paramount; true enough, cheap power is very important, almost essential, but certainly it is not everything. There have been cases where it was found much cheaper in the end to pay almost double for electric current in a certain locality than in another site not far distant from the first, for the simple reason that the cheaper power supply was hampered by frequent interruptions and expensive disturbances, which more than offset any possible saving in cost of power.

In further corroboration, it is well known that some of the most successful electrolytic soda manufacturers have found it to their advantage to sacrifice power by running their cells at decidedly higher voltage than is strictly necessary—which simply means consuming more power—and this in order to be able to use higher current densities, thereby increasing considerably the output of the same size

units, and thus economising on the general cost of plant operation. Here is one of the ever recurring instances in chemical manufacturing where it becomes more advantageous to sacrifice apparent theoretical efficiency in favour of industrial expediency.

All this does not diminish the fact that the larger electrochemical industries can only thrive where cheap power is available.

Modern progress of electrical engineering has given us the means to utilise so-called natural powers; until now, however, we have only availed ourselves of the water-power developed from rivers, lakes, and waterfalls. As far as larger electric power generation is concerned, the use of the wind, or the tide, or the heat of the sun, represents, up till now, nothing much beyond a mere hope of future possibilities.

In the meantime it so happens, unfortunately, that many of the most abundant water-powers of the world are situated in places of difficult access, far removed from the zone of possible utilisation.

But, precisely on this account, it would appear, at first sight, as if the United States, with some of her big water powers situated nearer to active centres of consumption, would be in an exceptionally favourable condition for the development of electrochemical industries. On closer examination we find, however, that the cost of water-power, as sold to manufacturers, is, in general, much higher than might have been expected; at any rate, it is considerably more expensive than the cost of electric power utilised in the Norway nitrate enterprises.

This is principally due to the fact that in the United States, water-power, before it is utilised by the electrolytic manufacturer, has already to pay one, two, and sometimes three profits, to as many intermediate interests, which act as so many middlemen between the original water-power and the consumer. Only in such instances as in Norway, where the electrochemical enterprise and the development of the water power are practically in the same hands, can electric current be calculated at its real cheapest cost.

Neither should the fact be overlooked that the best of our water-powers in the East are situated rather far inland. Although this does not matter much for the home market, it puts us at a decided disadvantage for the exportation of manufactured goods, in comparison again with Norway, where the electrolytic plants are situated quite close to a good sea-harbour open in all seasons.

Some electrochemical enterprises require cheap fuel just as much as cheap power; and, on this account, it has proved sometimes more advantageous to dispense entirely with water-power by generating gas for fuel as well as for power from cheap coal or still cheaper peat.

At present most of our ways of using coal are still cumbersome and wasteful, although several efficient methods have been developed which some day will probably be used almost exclusively, principally in such places where lower grades of cheap coal are obtainable.

I refer here particularly to the valuable pioneer work of that great industrial chemist, Mond, on cheap water-gas production, by the use of a limited amount of air in conjunction with water vapour.

More recently this process has been extended by Caro, Frank, and others, to the direct conversion of undried peat into fuel-gas.

By the use of these processes, peat or lower grades of coal, totally unsuitable for other purposes, containing, in some instances, as much as 60 to 70 per cent of incombustible constituents, can be used to good advantage in the production of fuel for power generation.

Whether Mond-gas will ever be found advantageous for distribution to long distances is questionable, because its heating value per cubic foot is rather less than that of ordinary water-gas, but this does not interfere with its efficient use in internal combustion engines.

In general our methods for producing or utilising gas in our cities do scant justice to the extended opportunities indicated by our newer knowledge.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 4, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Discontinuous Fluid Motion past a Bent Plane, with Special Reference to Aeroplane Problems." By Prof. G. H. BRYAN, F.R.S., and R. JONES.

The present investigation is based on the theory of discontinuous fluid motion, and in particular on the recent developments of that subject by Sir G. Greenhill. Its object is to obtain a hydrodynamical estimate of the effects of camber on the lift and drift of a lamina moving through a fluid, the motion being two-dimensional, and regarding the lamina as an aerofoil.

Instead of considering continuously curved laminæ, the investigation deals with laminæ the front and rear portions of which are plane but which meet at a dihedral angle. The method is applicable to surfaces with two or more bends.

After a suitable trigonometric transformation, the integrals forming the solution of the problem can be written in the form—

$$I_{1,3} = 2 \int_B^{90^\circ} \sin^2(U \pm \rho) \sin 2U \left\{ \frac{\sin(U+B)}{\sin(U-B)} \right\}^{\pm \frac{1}{2}} dU$$

the upper sign to be taken with the first suffix.

If  $\rho$  = density of fluid,  $Q$  = relative velocity of fluid and lamina,  $a$  a constant proportional to linear dimensions of the plane,  $\chi$  = exterior angle between the planes,  $B$  and  $\rho$ , the values of  $U$  at the bend, and, at the point where the stream divides, respectively then the solution of the problem is as follows:—

The length of the rear plane is  $I_{1,2}$ , the pressure on it  $\rho a Q(I_1 - I_3)/2$ , and the angle of attack  $2\rho + \frac{B}{\chi}$ . Similarly for the front plane.

It would not be possible to obtain a direct solution having given  $aI_1$ ,  $aI_2$ , and  $\chi$ , so the integrals have been calculated for different values of  $\rho$ ,  $B$ , and  $\chi$ . They can be evaluated by means of formulae of reduction, but the results are too complicated to be of use. Instead approximate methods have been employed. In applying these, Simpson's rules are inapplicable near  $U = B$ , so it seemed that the simplest way was to work out *ad initio* the formulae in the neighbourhood of  $B$ .

In the results, the total length of the planes has been kept constant (by varying  $a$ ) and different systems are compared, the object being to estimate the efficiency in respect of lift and drift, of surfaces in which the bend occurs at different distances from the front edge.

When  $\rho$  and  $B$  are small the angle of attack on the front plane is negative. This case is excluded from the present investigation.

The general conclusions are in agreement with experimental results, that a moderate degree of camber is beneficial in increasing the lift without a corresponding increase in drift.

"A New Type of Series in the Band Spectrum associated with Helium." By Prof. A. FOWLER, F.R.S.

The band spectrum associated with helium, as previously described by Curtis and Goldstein, includes bands with single heads and bands with double heads. A preliminary analysis of this spectrum has led to the following conclusions:—

1. The doublets do not follow the ordinary law of band spectra, but can be arranged in two series of the type hitherto exclusively associated with line spectra, and can be represented by the usual formulae involving the Rydberg constant. Nine bands of the main series and four of the second fainter series have been identified.

2. The two series may be likened to the principal and

diffuse series in the case of line spectra, but the usual relation between such series is not certainly indicated, and no equivalent of the sharp series has yet been traced.

3. The doublet separations are not in accordance with those associated with line spectra; they diminish in passing along the series, but do not vanish at the limit.

No regularity in the arrangement of the single bands has been recognised.

"Spectra of Ordinary Lead and Lead of Radio-active Origin." By T. R. MERTON.

Wave length measurements have been made of some of the principal spectrum lines of ordinary lead and the lead in pitchblende residues. It might reasonably be expected that small differences in the wave-lengths would be found, more especially in the case of any lines which belong to doublet or triplet series, since, according to the views of Prof. Hicks, an atomic weight term enters exactly into the separations of such doublets or triplets. No series have yet been discovered in the spectrum of lead, but it is probable that they exist, and an estimate of the order of the differences of wave-length to be expected according to Prof. Hicks's views is given.

No differences of this order have been observed, the spectra taken in juxtaposition showing no differences of wave-length, whilst the wave-length measurements of seven of the most prominent lines in the two leads agree to 0.03 A.U. A special comparison of the line  $\lambda = 4058$  A.U. with the interferometer shows that the wave-lengths of this line in the ordinary and radio-active lead are identical to within 0.003 A.U.

"Viscosity of the Vapour of Iodine." By A. O. RANKINE.

The paper records the method used by the author for measuring the viscosity of iodine vapour at four different temperatures ranging from 124° C. to 247° C. The basis of the method is the distillation of iodine from one vessel to another through a narrow capillary tube, the temperature of which could be varied. One of the vessels contains solid iodine, and is raised to 100° C., thereby establishing the driving pressure. The other vessel is immersed in a freezing mixture so that the iodine which is transpired as super-heated vapour is condensed there, the mass so transpired being determined by weighing the vessel which is removable.

The method gives, in repeated experiments, very consistent results, and the values obtained may be taken as accurate to about  $\frac{1}{2}$  per-cent. The range of temperature variation is not large enough to make the results suitable for testing the validity of Sutherland's formula, but it is found that they are, at any rate, not inconsistent with that formula. The values obtained are as follows:—

Temperature °C.	Viscosity in C.G.S. units $\times 10^4$ .
124.0	1.84
170.0	2.04
205.4	2.20
247.1	2.40

and Sutherland's constant  $C = 590$

In this paper the bearing of the results upon the empirical laws proposed previously by the author are also discussed.

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 3, 1915.

THE following were elected the Officers and Council for the ensuing year:—

President—A. Chaston Chapman.

Past-Presidents serving on the Council—Leonard Archbutt, Edward J. Bevan, Bernard Dyer, Thomas Fairley, Otto Hehner, R. R. Tatlock, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents—J. H. B. Jenkins, H. Droop Richmond, R. T. Thomson.

Hon. Treasurer—Edward Hinks.

Hon. Secretaries—P. A. Ellis Richards, E. Richards Bolton.

Other Members of Council—E. M. Chaplin, J. H. Coste, J. A. Dewhurst, P. V. Dupré, G. H. Gemmell, R. G. Grimwood, E. M. Hawkins, Charles A. Keane, Rudolf Lessing, L. Myddelton Nash, Thomas Tickle, W. Collingwood Williams.

Ordinary Meeting, February 3, 1915.

Mr. A. CHASTON CHAPMAN, President, in the chair.

Messrs. Harold Stanley Machin and Frederic Robinson were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Christopher William McHugo, 35, Warrior Square, Southend-on Sea; Cyril Joseph Heath Stock, County Analyst's Office, Darlington; George Tate, Windsor Buildings, George Street, Liverpool; and Thomas Edward Wallis, 5, Hillsborough Avenue, Exeter.

A certificate was read for the second time in favour of Mr. David Mitchell.

The following papers were read:—

"Determination of Sulphates in Flour." By G. D. ELSDON.

The author has examined many samples of plain and self-raising flour by the following method, which he has found accurate and fairly rapid:—Ten grms. of flour are added to 25 cc. of concentrated HCl contained in a 250 cc. beaker. The beaker is gently warmed for a short time, until all the flour has been attacked, and finally heated on the water-bath for about one hour. The liquid is diluted and filtered, and the sulphate estimated in the filtrate in the usual manner as  $\text{BaSO}_4$ .

The average amount of barium sulphate obtained in this manner from a genuine plain flour has been 3.5 mgrms., corresponding to 0.021 per cent of  $\text{CaSO}_4$ .

"General Principles Governing the Complete Analysis of Minerals and Ores." By W. R. SCHOLLER.

The author calls attention to the lack of published information on the subject of complete analysis, which he presents from a point of view of general applicability to ores, minerals, and intermediate products of inorganic and metallurgical industries.

#### ST. LOUIS ACADEMY OF SCIENCES.

At a meeting held on October 19, Prof. NIPHER gave an account of his work during the summer of 1914, at his summer place in Hessel, Mich., on "*Magnetic Disturbances in the Earth's Field due to Dynamite Explosions, Burning Black Powder, and the Fog-horn of a Steamer.*"

The magnetic needle was mounted on a frame of timber, the vertical posts of which were set 2 feet into the ground. The frame and the boxes containing the control magnets were loaded with half a ton of rocks. The boxes containing the control magnets were also clamped to the frame with large wooden clamps. The base of the air-tight vessel containing the magnetic needle was also clamped to the frame. The torsion head was braced by means of wooden bars. Four cords at right angles to each other were attached to the torsion head. They passed outward and downward through holes in the table, and upon them were hung two bars of wood at right angles to each other. These bars were also loaded with rock. The apparatus was protected from heat effects by a series of blankets within the tent, having air-spaces between.

No difficulty was found in producing marked local disturbances in the earth's field by means of dynamite suspended in air to the east and to the north of the tent. The needle being at right angles to the magnetic meridian, this disturbance indicated a variation in the horizontal intensity.

The amount of dynamite exploded varied from half a stick 6 or 8 feet from the tent to 30 sticks distant 275 feet. In the larger explosions, the sticks were placed end to end on bars of wood having a cross section  $1 \times 1\frac{1}{2}$  inch. Each stick of dynamite was securely held in place upon the bar by means of a winding of heavy cord. The ends of the bar suffered no appreciable injury. Those parts in contact with the dynamite vanished in dust so fine that it was difficult to find any trace of it. The changes in the position of the needle in explosions of this character amounted to ten or fifteen minutes of arc.

Much more marked effects were produced by distributing half a stick of dynamite into a column about 15 feet in length. It was packed closely into the angle of a little trough of wood, which rested upon a heavy beam of wood. The trough was held in position by means of masses of rock hung on cords. The column of dynamite was in line with the needle and either above or below the level of the needle. In this way deflections of about  $1^\circ$  of arc were produced. The direction of deflection was reversed by reversing the direction in which the explosion traversed the column. The end of the column nearest the needle was distant from it about 10 feet.

This seems to indicate that a magnetic field is created around this exploding column, like that which exists around a wire conductor carrying a current of electricity. In most of the experiments of this character only a small part of the column exploded. It is believed that the conditions which will cause an explosion of the entire column with equal violence throughout have been finally attained, and this work will be continued.

The black powder was spread over a platform having an area of 25 square feet, placed a few feet from the west side of the tent. The amount of powder spread over the platform was from 25 to 50 pounds. The flame shot upward to a height of 15 to 30 feet. The lines of the earth's field were deflected around the region filled by this flame. The intensity of field within the tent was momentarily increased. The deflection of the needle amounted to from twenty-five to fifty minutes of arc.

At the request of Prof. Nipher, the captains of the steamers of the Arnold Transit Co. were instructed by the President, Mr. Geo. T. Arnold, to blow a loud and prolonged blast on their fog-horns when at the nearest point to the observing station. This distance was about half a mile. Appreciable effects was thus produced when the air was quiet, the sky was clear, and the intensity of the field had reached a high value. The result in every case was to decrease the intensity of the earth's field.

In two cases the blast from the 5 o'clock boat was at once followed by a premature appearance of the sunset disturbance. Rhythmical vibrations over from  $10^\circ$  to  $20^\circ$  of arc at once followed and continued for four or five minutes. This result needs further examination under more favourable conditions.—*Science*, N.S., xl, p. 108.

action is treated considerably more fully than before. The book has a high value for the student of medicine, as containing in one volume all that he wants and no more. The arrangement of the material is good, and the theoretical aspects of the subject and general principles are always very clearly treated. The section on practical chemistry contains some typical preparations of substances which are included in the syllabus of the Examining Board, an outline of qualitative analysis, and a very short treatment of quantitative analysis, including only one gravimetric estimation, that of a sulphate, and a few volumetric processes.

*Appendices to the Thirty-eighth Annual Report of His Majesty's Inspectors of Explosives.* London: Wyman and Sons, Ltd. 1914.

The appendices to the report of His Majesty's Inspectors of Explosives contain lists of authorised explosives, details of the importation of explosives during 1913, and tabular statements showing the accidents by fire or explosives which came under the notice of the Home Office during 1913. Lists are also given of the special reports which have been issued and of prosecutions under the Explosives Act.

*Annuaire pour l'An 1915.* ("Annual for the Year 1915"). Paris: Gauthier-Villars et Cie.

This annual contains copious tables of astronomical and spectroscopic data, and also much information relating to geography, meteorology, and statistics. Many useful tables are given for the benefit of the mathematician and physicist, and in addition the annual contains a long and interesting article by M. G. Bigourdan on the examination of mirrors and objectives and the different parts of telescopes. This article is comprehensive and detailed, and is well illustrated by diagrams.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 2, January 11, 1915.

**Molecular Weights of Oxybenzoic Acids.**—Chesner de Coninck.—The molecular weight of salicylic acid can be determined by the analysis of its calcium and ammonium salts. The former is dissolved in warm water, the solution is treated with potassium carbonate, and the lime determined as  $\text{CaCO}_3$ . The ammonium salt is decomposed by soda, and the ammonium is determined by a titrated solution of sulphuric acid. The ammonium salts of the meta- and para-oxybenzoic acids can be analysed similarly. The mean of the results obtained is 137.986.

## MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Royal Society of Arts, 8 (Fothergill Lecture). "Motor Fuels," by Prof. V. B. Lewis.
- TUESDAY, 23rd.—Royal Institution, 3 "Muscle in the Service of Nerve," by Prof. C. S. Sherrington, F.R.S.
- WEDNESDAY, 24th.—Royal Society of Arts, 8. "The Economics of War," by W. J. Ashley, M.A.
- THURSDAY, 25th.—Royal Institution, 3. "Zoological Studies—War and Evolution, Nations as Species," by P. Chalmers Mitchell, F.R.S.
- FRIDAY, 26th.—Royal Institution, 9. "The Solar Eclipse of 1914," by The Rev. A. L. Cortie, F.R.A.S., &c.  
Physical 5. "Magnetic Character Figures, Antarctic and International," by C. Chree. "Electrification of Surfaces as affected by Heat," by F. H. Shaw. "Electromagnetic Inertia and Atomic Weight," by J. W. Nicholson.
- SATURDAY, 27th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

## NOTICES OF BOOKS.

*A Manual of Chemistry.* By ARTHUR P. LUFF, M.D., B.Sc.Lond., F.R.C.P., F.I.C., and HUGH C. H. CANDY, B.A., B.Sc.Lond., F.I.C. Fifth Edition. London, New York, Toronto, and Melbourne: Cassell and Co., Ltd. 1915.

The general plan of this book remains unaltered in the fifth edition, but many additions have been made to the text. The discussion of the theory of ionisation, for example, has been much enlarged, and the law of mass



# THE CHEMICAL NEWS.

VOL. CXL., No. 2883.

## THE WAR AND BRITISH ECONOMIC POLICY.

### THE ANILINE DYE INDUSTRY.

IN view of the urgency of the aniline dye question, and the discussion which is now taking place on the Government scheme, it has been thought expedient to issue at once Part IV. of a Memorandum dealing with the entire question of "The War and British Economic Policy," published by Messrs. P. S. King and Son, of Westminster. This part of the Memorandum is devoted to the consideration of the dye industry, and the following is an abridgement of some portions of it:—

British industries use annually dyes to the value of nearly £2½ millions. Of this total about £1½ millions came from Germany, about £150,000 from Switzerland, and only about £200,000 was of British home production. In 1913 the United Kingdom exported coal-tar dye-stuffs to the value of £177,000, of which £20,000 went to Germany. Aniline dyes constitute an indispensable material in many branches of the textile, leather, paper, and other trades, and the annual value of the goods in which aniline dyes are an essential or important material is estimated to be £200 millions.

The opinions of a large number of firms interested as users or manufacturers of aniline dyes on the British industry and its resources may be summarised as follows:—It is fully recognised on all sides that the dependence upon German supplies is so great that the present capacity of dyeworks is totally inadequate to fill the gap, and it is evident that an enormous new industry, requiring great capital expenditure, must be created. It is almost universally agreed that the fear of renewed German competition after the war constitutes an apparently insuperable hindrance to the raising of this capital. One firm of tweed and costume cloth manufacturers, for example, states that "to ask firms to invest money in plant without an assurance from the Government that they will be protected from undue competition at the termination of the war is not a commercial proposition." It is pointed out by several firms that the heavy excise duty on alcohol severely hampered the development of the British dye industry until recent years, and even now it is felt that some further Government aid in this respect is needed. The great desire for reform in the matter of patents is also emphasised. One firm suggests that there would be no lack of capital or enterprise "if we had the necessary knowledge," and another firm states their opinion that the British colours are not as strong or as fast as the German make. It is, however, the absence of security against German or Austrian competition when the war is over that constitutes the root difficulty.

The war demand in the textile industries has relaxed the immediate stringency, inasmuch as many factories whose normal productions required a considerable variety of dyes are now making khaki and other textile requisites for war in regard to which the dye difficulty has been overcome.

To meet the situation the Government first proposed to subsidise the establishment of a British dye industry by the creation of a new joint-stock company to increase the output of existing dyeworks. The company was to have a working capital of £4½ millions, of which £3 millions was to have been subscribed by the public (principally the dye-users), and £1½ millions by the Government in the shape of a loan bearing interest at 4 per cent. This scheme did not prove acceptable to the public, chiefly because of the absence of security for the investor against German com-

petition after the war. A second Government scheme has now been propounded. It provides for an original share capital of £2 millions, of which in the first instance £1 million would be issued. The Government is prepared to advance £1 for every £1 of share capital raised, up to a maximum of £1 million. Should it be subsequently found necessary the Government will further contribute £1 (up to a maximum of £500,000) for every £4 further share capital raised. The effect of this arrangement will be that if full advantage be taken of the Government offer, the company will ultimately have a share capital of £3 millions and a loan capital of £1½ millions. The Government advance will bear interest at the rate of 4 per cent, and be repayable within twenty-five years. The payment of interest will be non-cumulative for the first five years and there will be no compulsory sinking fund. The interest on the ordinary shares will be limited to 6 per cent per annum so long as any part of the Government's advance is outstanding. Further, with a view to the promotion of research, the Government have undertaken to make a grant to the company during a period of ten years of a sum not exceeding in the aggregate £100,000 to be devoted exclusively to experimental and laboratory work. An option has already been obtained for the acquisition by the company of important dye-making works, and negotiations for other options of the kind are in progress, and there is reason to believe that satisfactory arrangements can be made with important producers in Switzerland. The scheme, like the original scheme, provides for the nomination by the Government, as long as any part of the Government advance is outstanding, of two directors who will have the ordinary powers of directors, and also certain special powers to prevent undue preference or encroachment on the business of undertakings not concerned with the making of dyes and colours. The agreement to be made between consumers of dyes and the company has been modified, and will, it is believed, be more acceptable to consumers than before. The consideration for this agreement is the supply by the company to the customer of certain of the dyes required by the customer during the continuance of the present war. The customer undertakes for a period of not less than five years to purchase from the company all dyes which he may require, and the company can supply, and not to purchase dyes elsewhere. The prices shall be reasonable prices to be fixed from time to time by the Directors of the Company.

There are many questions to be decided about the scheme as a whole. For example, what dyes will the company manufacture, and who will decide what dyes it may and shall make? What prospect is there of satisfying the "consideration" that the dyes required by the customer will be provided by the company during the war, and what is to happen if the company fails in this respect? Is there an obligation on the company to provide any dye that the user requires, whether its production is likely to be profitable or not to the company? What are "reasonable prices," and is it essential that these prices shall be profitable to the company? The points for immediate consideration are (a) whether this revised scheme will secure the necessary support of the interests concerned; (b) whether the dyes would be forthcoming in time to meet the approaching exhaustion of all available supplies; (c) what are the potentialities of the existing British chemical and allied trades at the present time; (d) whether the present Government scheme is likely to make the most of these potentialities, and if not whether other means can be devised for achieving the object in view. The evidence received by the Tariff Commission from the leading firms of makers and users of dyes in the United Kingdom goes to show that the potentialities of the country are sufficient to relieve any feelings of apprehension, if the resources of British industry are properly organised and an adequate guarantee as to the future is given. The general trend of the evidence received is that no guarantee would be considered adequate which did not include protection for the new industry.

## THE SOLIDIFYING POINT OF MUTTON TALLOW.

(II.).

By ROBERT MELDRUM.

THE author has already demonstrated (CHEMICAL NEWS, cix., No. 2827) that mutton and beef tallow do not possess a constant solidifying point for any given sample, and that solidification takes place 8° C. below the melting-point. Also, previous to solidification, the thermometer falls to 12° C. below the melting-point. This characteristic property is common to all mixtures of solid and liquid glycerides, but does not hold good for mixtures of solid and liquid fatty acids. The author has also demonstrated that the melting-point of a mixture of solid and liquid glycerides is equal to the melting-point and solidifying point of their fatty acids, thus showing that with the glycerides solidification takes place below normal for some unknown causes. Despretz cooled water 20° C., and Regnault cooled glacial acetic acid 26° C. below normal melting-point without solidification taking place. Also, parabromophenol with melting-point of 64° C., may be cooled to 13° C. without solidifying. Also, thymol with melting-point of 44° C., may be cooled to 16° C. and lower, and maintained in this state for prolonged periods without becoming solid. In these cases when solidification does take place the temperature always rises to the normal melting point. But such is not the case with the glycerides, as these when supercooled about 12° C. below melting-point solidification takes place some 8° C. below normal. With mixtures of stearic and oleic acid the author has shown (CHEMICAL NEWS, vol. cviii., No. 2813) that supercooling is present during solidification, which lowers the point of solidification by 1° C. That this supercooling is present more or less in all solidifications is apparently beyond doubt, and that it is present to a very marked degree in the glycerides is evident.

With the view of investigating the disturbing influence of the liquid glycerides in tallow on the solidifying-point these were removed by means of ether. 200 grms. of tallow were finely shredded and digested with 200 cc. ether, the ether extract pressed through filter-cloth, and the residue melted till free from ether. This was repeated three times. The product obtained was a hard, semi-transparent, and very white stearin free from moisture, free fatty acids, free glycerin, but still containing some liquid glycerides. The solidifying point was determined by Dalican's method, the glycerides being melted at 80° C. and stirred to the indicated temperatures, then the thermometer fixed  $\frac{1}{2}$  in. from bottom of tube and readings made.

Cooled by stirring to °C. . . . 55 49 48 55 47  
Solidifying point + rise, °C. . . 49.8 50.3 51 49.7 50.4  
Rise, °C. . . . . 3.4 4.0 3.6 3.8 3.9

*Influence of Suspended Matter.*

During the above tests it was observed that the melted glycerides contained a little suspended matter. The fat was therefore refiltered and another series of solidifications made with following results:—

Cooled by stirring to °C. . . . 50 47 47 55 52  
Solidifying point + rise, °C. . . 49.8 50.6 50.7 50.1 50.1  
Rise, °C. . . . . 4.6 3.8 3.9 5.2 4.4

It is clear the presence of suspended matter has no effect on the erratic setting and "rises."

*Secondary Stationary Points.*

As Chittenden and Smith have shown that tristearins exist with melting points of 52° C., 64.2° C., and 69.77° C., the thermometer therefore during the above experiments was in each case carefully examined for a second stationary point, but without success. During both the fall

and rise every tenth of a degree of difference was closely watched, and after solidification the thermometer was examined during a fall of 6° C., but with the same result. It is, therefore, apparent that the glycerides have only one solidifying point.

*Solidifying Phenomena.*

In the course of the above experiments, and those with the tallow itself, it was observed that the fat began crystallising at bottom of tube from which ascended a column of opaque fat around thermometer bulb. This is more or less constant in its character, and takes place about 47° C., and as cooling proceeds the cloud extends to sides of tube. The theory was advanced that the ascension of this cloudy column of fat had some relation to erratic setting. When the stearin is melted at 80° C. and allowed to cool to 55° C., and then stirred in a circular direction, it was found that temperature of column of liquid fat is not uniform, the temperature increasing from bottom upwards by 5° C. This circular method of mixing to produce a uniform temperature in the tube is the usual method employed in solidification tests, and may have some relation to the erratic setting of the glycerides. But with stearic acid, spermaceti, paraffin wax, and naphthalene, though circular stirring be employed, and where the temperature of melt must also be variable throughout its length, constant results are obtained. The following tests were made by melting the glycerides at 80° C., allowing to cool till crystals appeared at bottom of tube, and then mixing by churning up and down with wire stirrer and fixing thermometer.

Solidifying point + rise, °C. 50.4 50.1 50.1 50.7 51.0  
Rise, °C. . . . . 3.9 5.2 4.4 4.5 4.2

The fat, therefore, whether at a uniform temperature or not throughout its mass, makes little or no difference in results obtained.

*Comparison of Solid Glycerides with Tallow.*

The following is a comparison of the solid glycerides and the tallow from which it was prepared:—

	Solid glycerides.	Tallow.
Variation in "rise," °C. . . . .	1.8	3.8
Variation in "zero," °C. . . . .	2.5	5.5
Variation in solidifying point, °C. . . . .	1.3	3.0
Average "rise," °C. . . . .	4.2	2.4
Average solidifying point, °C. . . . .	50.3	41.1
Average melting-point, °C. . . . .	53.8	48.4
Ratio-melting and solidifying point, °C. . . . .	3.5	7.3

From the above it will be seen that variation of the "zero," solidifying point and "rise" is nearly 100 per cent less than with the tallow, thus showing that the presence of liquid glycerides influence to a considerable extent erratic solidification, or in other words solid glycerides yield more constant results than do mixtures of solid and liquid ones. It will be noted that the solid glycerides yield "rises" twice as great as the tallow. Apparently the "rise" increases with increasing solidifying point, and points to the fact that the solid glycerides possess supercooling properties to a marked degree. Again, there is closer agreement between melting and solidifying point as the melting-point increases, showing the disturbing effect of the liquid glycerides. From this it appears the erratic behaviour in the setting of mixtures is due to supercooling effect in the solid glycerides and which is intensified by dilution with liquid ones.

*Elimination of Low Zero and "Rise."*

Attempts were made to eliminate the low zero-point, the temperature to which the thermometer falls before commencing to "rise," and with success, as will be seen from the following experiments.

*Experiment No. 1.*

Melted the stearin in test-tube at 70° C., and placed in melting-point apparatus with hot water-jacket. The water in jacket was constantly stirred and the temperature lowered slowly. The stearin was also stirred with thermometer, the water jacket being maintained about 1° C. lower than the fat.

70° C. }  
60° C. } Quite fluid and clear; five minutes.  
50° C. }  
45° C. Cloudy, but quite fluid.  
44° C. Cloudy, but quite fluid; rises.  
49.4° C. Thermometer rises to.

*Experiment No. 2.*

Maintained melted stearin at 51.5° C. in water-jacket at same temperature for two hours, both being stirred. Solidifies gradually to soft pasty solid, which latterly becomes too rigid to stir. Thermometer rises to 52.1° C. The cause of solidification at this temperature and under these conditions is very curious. What actually takes place is this:—As the fat is stirred at 51.5° C. the surface of stearin in tube becomes coated with a film of solid fat which the stirring disperses through the molten fat, but which does not become melted, and causes the liquid fat to gradually become very opaque. The opacity increases with duration of stirring till the whole mass is solid. The setting of the fat here takes place by surface films, the formation of these being due to contact with the colder air in tube. The films accumulate in the melted fat till spontaneous crystallisation takes place. On raising temperature complete clarification does not ensue at 53° C., but takes place on increasing to 56° C., this being the apparent melting-point by this method.

*Experiment No. 3.*

If solidification takes place at 52.1° C. with only a "rise" of 0.6° C. under the above conditions, then theory would require that when cooled to 51.5° C. and some solid fat added, and dispersed through the mass, solidification ought to take place at that temperature with a low "rise." To the clear melted fat at 53° C. was added about 2 grms. granulated sample, and this dispersed through the mass and slowly stirred, and temperature allowed to fall to 52° C., and maintained at this for ten minutes. Thermometer fell to 51.7° C., and rose to 52.3° C., the solidification gradually gaining in solidity. On melting opacity does not disappear till 56° C. is reached.

*Experiment No. 4.*

Attempts were made to solidify at 60°, 57°, 55°, and 53° by adding granulated stearin at these respective temperatures and maintaining same for fifteen minutes, but with negative results. On reducing temperature to 50.5° C. thermometer rose to 51.7° C., and on heating opacity disappeared at 56° C.

The results of the above experiments are as follows:—

Solidifying point + rise, °C.	..	52.1	52.3	51.7
Rise, °C.	..	0.6	0.6	1.2
Melting-point (opacity method), °C.		56	56	56

From the above tests it will be seen how the "rise" and "zero" point tend to vanish with increase in solidifying point. As the "rise" is decreased to the extent of 3.4° C. the solidifying point increases by nearly 2° C. There is no doubt that under more exacting thermal conditions the "rise" and "zero" point would be extinguished in all solid glycerides and mixtures of same, and in many other compounds where a "rise" takes place. The author has found that a rise is absent in the setting of paraffin-wax, ozokerite, spermaceti, bees-wax, naphthalene, and many other compounds, and when present is no doubt due to supercooling influences. Based on the evidence of the "rise" it would appear the actual solidifying point is higher

than 52.3° C., which is confirmed by the melting-point and the variation of the solidifying point under these exacting conditions.

*Melting-point of Solid Glycerides.*

Capillary tube method—

Plug fat ascends, °C.	..	52.2	54.1	53.8	53.5
Plug fat clarifies, °C.	..	54.4	54.4	54.4	55.2

Thermometer bulb method—

Drop appears, °C.	..	53.2	54.3	53.8	54.3
Drop off, °C.	..	53.6	56.0	54.1	54.4

As the author has previously pointed out these melting-point methods leave much to be desired and have inherent failings as regards accuracy. This is confirmed by ascertained maximum difference between above readings, which amounts to 2.1° C., and also by the melting-point by the opacity method, which is 56° C.

*Summary.*

The solid glycerides used in the above experiments are no doubt a mixture of tristearin and tripalmitin with a little triolein, and a comparison with the tallow from which they were obtained clearly demonstrates the powerful modifying influences of the olein on erratic solidification. With mixtures of stearic acid and oleic acid in all proportions this disturbing factor is absent, there being a close agreement within 1° C. between solidifying and melting-point. Then, again, as the writer has previously shown, the melting point of tallow and its fatty acids and solidifying point of acids are all constants, therefore erratic solidification cannot be explained on the basis of double combinations of triolein and tristearin or tripalmitin. The same remarks hold good for the isomorphous theory of Chittenden that tripalmitin and tristearin exist in three separate modifications with variable and definite melting and solidifying points depending on the previous heat treatment of the fat. Nor can the author's theory previously put forward as to rapid changes in density and viscosity at the critical point be accepted to account for these facts. Based on the above experiments the true explanation is most likely that fluctuations in the melting-point are due to errors in manipulation and observation, and fluctuations in solidifying point are due to speed of crystallisation. The experiments point to the fact that if the amount crystallised per unit of time remained constant the solidifying point would also be constant with its accompanying "rise." The mono-, di-, and triglycerides of palmitic and stearic acids, and no doubt all other glycerides, appear to require supercooling to start rapid crystallisation, and are characteristic of these fatty compounds. For each glyceride there appears to be a specific temperature to which, when supercooled, solidification commences, or as the author defines this as the "zero" point. This supercooling effect is common to many organic and inorganic compounds, solutions, and mixtures of same, and is no doubt the cause of much perplexity in innumerable published melting and solidifying points of fatty acids, organic salts, and particularly the waxes and solid fats.

The most interesting problem which presents itself in the solidification of the glycerides is failure to attain their normal solidifying point when supercooled. This apparently pointing to the fact that the melting has lowered the solidifying point, through some molecular change. This theory appears almost convincing when we take into account the general facts that with water, acetic acid, and many other substances when supercooled, the temperature rises to the normal solidifying point. But with the glycerides solidification takes place below normal. As the "rise" is rapid and considerable, crystallisation must be rapid at the supercooled temperature, and a normal and constant solidifying point ought to result. The true explanation of this is a purely thermal one. The latent heat of fusion is not sufficient to raise the supercooled mass to the normal solidifying point, the more so when mixtures of solids and liquids are dealt with.

GOVERNMENT CO-OPERATION WITH  
INDUSTRIES.\*

If the war will teach us the value of industrial research as an aid in the development of our industries, if it will induce manufacturers to engage technologists to devise processes for manufacturing the goods which hitherto they have purchased abroad, if it will open up foreign markets hitherto closed to us, it may prove a national benefaction. But unless the economic conditions are right it may not pay to spend millions in scientific investigation and in building factories. Economic conditions are, in part, controlled by governments, and it is the purpose of this article to discover whether or not our Government is enabling American capitalists to make the most of the opportunities created by the present conflict.

Perhaps the most conspicuous example of our apparent indifference to industrial research is to be found in the chemical industry—at least the newspapers told us so.

*What the Establishment of a Coal-tar Chemical Industry Means.*

Since the American chemical industry has been more severely criticised than any other, we may well enter into a discussion of its difficulties, bearing in mind that they apply in a lesser degree to other manufacturing activities. There was a wild scurrying about for dyes and chemicals last August. Textile manufacturers bought all the colours that they could carry in stock. Certain chemicals, particularly some pharmaceutical products, were sold at a great advance over prices which, even in time of peace, were considered too high. The newspapers took up the question, and rather hysterically accused American chemists of incompetence. We had built up a great steel industry, a great machine tool industry, a great automobile industry. Why hadn't we built up a great chemical industry? Because Germany had a chemical monopoly, because the whole structure of modern organic industrial chemistry is German, it was thought that the German mind must be endowed with some magical power of penetration not given to the American, British, or French intellect.

*Why Government Co-operation is Necessary.*

It is this wonderful industry is to be established in this country it can only be with Governmental co-operation. An economic balance must be maintained, production must be carefully watched, wasteful competition must be checked, prices must be fixed by agreement on some products so that the whole enterprise may flourish. The slightest change from one of the operations may serve to upset this economic balance. In a word, only a trust with the power to control production and the market could establish a great coal-dye industry in America—the very piece of business machinery which is most abhorred in Washington. The huge chemical firms of Germany are knit together, more or less, in a combination which is able to dominate the markets of the world, and which exists not only with Governmental sanction and under Governmental control, but to a certain extent with Governmental encouragement. If we are to compete with Germany we must employ the same economic weapons.

The Special Committee appointed by the New York Section of the American Chemical Society to study the chemical situation arrived at the conclusion that "alterations in our tariff law are inevitable" if we are to have a coal-tar chemical industry. The nation as a whole must bear the burden of expanding industrial chemistry in this country. Private capital can do no more than it has done. German plants cannot be valued exactly. They must be worth several hundred million dollars. Since they were built decades ago most of them have long since been paid for in profits. Couple to that financial advantage the permission to use such co operative commercial devices as pools and selling agreements, and we need no longer wonder why,

under present conditions, we are not likely to have a chemical industry comparable with that of Germany. A protective tariff would not place us altogether on a par with Germany; but it would at least make it profitable to engage in a few chemical activities.

We cite the coal-tar chemical industry because it is the most glaring example of the need of Government co-operation that we can find. The difficulties of establishing that industry are found in a lesser degree in other industries. But everywhere the German trust looms large.

*The Futility of Half-way Measures.*

As matters now stand it is doubtful if, under the Clayton law, a group of competing American manufacturers could even engage a common selling agent to introduce their goods in foreign markets—so completely have we tied their hands.

Thanks to the Clayton law, still judicially unconstrued, our great manufacturing corporations may not legitimately use the powerful machinery of combination in their struggle for foreign recognition. A new enterprise which is to be conducted on the large scale of the German coal-tar chemical industry, for example, cannot now be started in this country. No capitalist would be fool enough to engage in it, without knowing how far he could meet German competition with its own weapons in home and foreign markets. Where, then, is the incentive to spend fortunes in industrial research, in establishing highly ramified channels of distribution, in building up industries which could not long withstand the attacks of a formidable and enterprising foreign competitor who is permitted to use the very implements which our Government has snatched from our hands?

We are not pleading here for a return to the old days when trusts held us in the hollow of their hands, but we are pleading for a judicious and controlled use of the economic advantages that accrue from production and distribution on a large scale. The trust and the cartel are not unmixed blessings for Germany; but so long as they play a predominant part in forcing us out of foreign markets, so long as they are supported by a paternal government as part of a well-planned scheme for German commercial expansion, so long will it be impossible for us to build up great industries dependent on foreign markets as an outlet for surplus products.

AN IMPROVEMENT OF THE BARIUM  
SULPHATE DETERMINATION OF SULPHUR IN  
SOLUBLE SULPHATES WHEN SODIUM  
SALTS ARE PRESENT.

By W. A. TURNER.

WHEN barium sulphate is precipitated by the reaction between a soluble barium salt and a soluble alkali sulphate, or in presence of large quantities of alkali salts, there is likely to be, as is well known, considerable contamination of the precipitate. Alkali sulphates and barium chloride may be found in the ignited sulphate, while hydrochloric and sulphuric acids may be volatilised in the ignition (Hulett and Duschak, *Zeit. Anorg. Chem.*, 1904, xl., 196; Allen and Johnston, *Journ. Am. Chem. Soc.*, 1920, xxxii., 588; Johnston and Adams, *Ibid.*, 1911, xxxii., 829). If the precipitation is made with the object of determining barium, the ignited precipitate may be dissolved in hot concentrated sulphuric acid, recovered in crystalline form by evaporation of the sulphuric acid, filtered, washed free from impurities, ignited, and weighed in a satisfactory condition of purity (Mar, *Am. Journ. Sci.*, 1891, [3], xli., 288; Gooch and Hill, *Ibid.*, 1913, [4], xxxv., 311). The precipitate formed by an excess of barium chloride, for the purpose of determining the sulphate ion, and contaminated by that reagent, cannot,

\* Abstracted from an article in *Scientific American*, Jan. 30, 1915.

however, be purified by re-crystallisation from sulphuric acid, since, in this action, the included barium chloride is converted to barium sulphate, and added to the amount which represents the sulphate ion to be determined. The magnitude of the error encountered is largely dependent upon the conditions under which the determination is made. While the method may be modified so as to reduce one source of error to a minimum, the same modification may increase another source of error, so that the final result is not satisfactory. In an exhaustive study of the sources of error and the influence of various factors on them, Allen and Johnston, and Johnston and Adams (*loc. cit.*), find no method of eliminating the observed phenomena, but by making a series of corrections are able to derive results which are accurate, or nearly accurate.

The investigation of which this paper is an account was directed to the elimination of error, due to the incomplete formation of the insoluble barium sulphate, by removing the alkali salts in a preliminary treatment with hydrochloric acid.

It appeared in preliminary experimentation that the determination of the sulphate ion of pure copper sulphate by precipitating with barium chloride, added (as is usual) in dilute solution, and gradually to the hot solution of the copper salt, yields results very near the theory—the tendency of the barium sulphate to carry with it another sulphate, by inclusion or combination, being much less marked in the case of copper sulphate than in the case of the alkali sulphates. (Allen and Johnston, *loc. cit.*, find this to be true also of the sulphate of another bivalent element, viz., magnesium). For the experiments to be described, the copper sulphate was prepared by twice crystallising the presumably pure (chemically pure) salt from the hot water solution while stirring vigorously to promote the separation of the substance in finely-divided form. These crystals dried in air for two days gave, on analysis, the results shown in Table I.

These results are obviously very close to theory, but it is not improbable that in them some slight tendency toward the carrying down of copper sulphate with the barium sulphate may have been counteracted by the inevitable inclusion of traces of barium chloride. (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxi., 67; *Zeit. Anorg. Chem.*, 1895, viii., 473).

Upon making the precipitation under exactly similar conditions, excepting the presence of alkali salts, the error due to the carrying down of unconverted alkali sulphate is at once made evident by the error of deficiency. This is shown in the results of Table II.

The next step was the attempt to eliminate the error, due to incomplete conversion of the alkali sulphate, by the preliminary precipitation and removal of the alkali chloride. An accurately weighed portion of copper sulphate with an approximately known weight of alkali chloride was dissolved in a small amount (25 cc.) of water, the solution saturated with gaseous hydrogen chloride, the precipitated alkali chloride filtered off on asbestos in the perforated crucible, and washed with concentrated hydrochloric acid. The filtrate was evaporated on the steam-bath (after dilution with an equal volume of water to prevent mechanical loss during the evaporation), the residue diluted, filtered (to remove possible traces of silica derived from the glass container), acidified with 1 cc. of 4 per cent hydrochloric acid, and treated as before, at a volume of 350 cc., with barium chloride. The results are given in Table III.

In this process the negative error of the former process, due to incomplete conversion of the soluble sulphate to barium sulphate, is eliminated and replaced by a positive error which can only be due to the inclusion of foreign matter, either barium chloride, or, possibly, a trace of silica, derived from the glass during the long evaporation of the hydrochloric acid solution, and not completely removed by one dehydration and filtration.

In the following set of experiments aqueous hydrochloric acid was substituted for the gaseous acid, and the precipitation of the sodium chloride was made by adding to the concentrated solution of the weighed copper sulphate and sodium chloride (about 10 cc.), approximately five times its volume of the concentrated acid; the precipitated chloride was filtered off, and the solution further treated as described above. The results of this treatment are given in Table IV.

It is to be seen that very fair results—very probably due, however, to a balance between the now largely reduced error due to incomplete conversion of the soluble alkali sulphate into barium sulphate, and a small error due to inclusion of foreign matter—are obtained by the use of concentrated aqueous hydrochloric acid to remove the sodium salt. Experiments in which the removal of potassium chloride was similarly attempted were not equally successful, no doubt on account of the greater solubility of potassium chloride in hydrochloric acid and the greater tendency of the barium sulphate to carry down the unconverted potassium sulphate.

This method of eliminating the effect of sodium salts in the precipitation of barium sulphate would seem to have some application in the analysis of sulphides and insoluble substances where fusion with sodium carbonate is necessary. Where sodium carbonate and potassium nitrate are ordinarily used, sodium carbonate and sodium peroxide may be substituted so that only sodium salts need be removed by the treatment with hydrochloric acid.

Whenever the sulphate ion is to be determined by precipitation as barium sulphate from a solution containing sodium salts the results of the analysis may be very much improved by the removal of the sodium before precipitating the barium sulphate. The method suggested may be summarised as follows:—

The substance, representing about 1 grm. of barium sulphate, is dissolved (after fusion, if necessary, with sodium carbonate and sodium peroxide) in the least convenient quantity of water. It is then treated with five volumes of concentrated hydrochloric acid and the resulting precipitate of alkali chloride is filtered off on asbestos in a perforated crucible, by the aid of suction, into a beaker under a bell-jar. After the precipitate of alkali chloride has been completely washed by concentrated hydrochloric acid contained in a gravity wash-bottle, the filtrate and washings, diluted with an equal volume of water, are evaporated to dryness on the steam-bath, the residue taken

TABLE I.—Analysis of Pure Copper Sulphate.

No. of CuSO <sub>4</sub> ·5H <sub>2</sub> O expt. found.	BaSO <sub>4</sub> found. Grm.	Theory for BaSO <sub>4</sub> . Grm.	Error in terms of BaSO <sub>4</sub> . Grm.	Error in terms of -SO <sub>3</sub> . Grm.	Per cent.
1. 1'1668	1'0904	1 0911	-0'0007	-0 0003	-0'03
2. 1'5373	1'4383	1'4375	+0'0008	+0 0003	+0'02
3. 0 9042	0 8453	0 8455	-0 0002	-0 0001	-0'01
4. 1'3812	1'2906	1'2915	-0 0009	-0'0004	-0'03

TABLE II.

5 grms. NaCl added in Experiment No. 1.

	5 " KCl	" "	No. 2.
1. 1'0879	1'0049	1'0173	-0'0124
2. 1'4371	1'3154	1 3450	-0'0296

TABLE III.

3 grms. Sodium Chloride added in each Experiment.

1. 0 9774	0 9196	0 9139	+0'0057	+0'0024	+0'26
2. 1'0976	1 0345	1 0263	+0'0062	+0'0025	+0'25
3. 1'3255	1'2444	1'2395	+0'0049	+0 0020	+0 16
4. 1'2855	1'2057	1'2021	+0'0036	+0 0015	+0 12

TABLE IV.

3 grms. Sodium Chloride added in each Experiment.

1. 0'8444	0 7912	0'7896	+0'0016	+0'0006	+0'08
2. 0 9775	0'9145	0'9141	+0'0004	+0'0002	+0 02
3. 0'9801	0 9158	0'9165	-0'0007	-0'0003	-0 03
4. 1'3620	1'2742	1'2736	+0'0006	+0'0002	+0'01



up with a little water and 1 cc. of 4 per cent hydrochloric acid, and then filtered through a small filter. The solution is then diluted to 350 cc., heated to boiling, and a slight excess (1 to 2 cc.) 10 per cent barium chloride solution added drop by drop from a burette. The precipitate is allowed to digest on the steam bath for some hours, over-night if convenient, and then filtered on the perforated crucible, ignited at low red heat, and weighed.

To Prof. F. A. Gooch my thanks are due for kindly assistance and counsel in carrying out this work.—*American Journal of Science*, xxxviii., p. 41.

## ON THE ACTION OF LEAD, COPPER, TIN, NICKEL, ZINC, AND ALUMINIUM ON WATER.

By Dr. W. P. JORISSEN, The University, Leiden, Holland.

(Concluded from p. 92).

### 14. Copper.

SOME general remarks on the corrosion of copper by dilute sulphuric acid in the presence of air have been made on p. 57. Here it may be mentioned that hydrogen peroxide is formed in this process, according to M. Traube's observations (Note 95). Sackur and Mauz (Note 96) observed that the rate of dissolving increased with the velocity of the current of air drawn through the solution and with the concentration of the acid. As the equilibrium  $\text{Cu} + 2\text{H}^+ \rightleftharpoons \text{Cu}^{++} + \text{H}_2$  is instantly reached according to Nernst, the rate of dissolving will only depend on the rate of oxidation of the hydrogen and on the speed of diffusion of the Cu-ions from the boundary layer and of oxygen and H-ions towards it. Cl-ions appear to have an accelerating influence on the rate of dissolving.

Ohlmüller and Heise (Note 97) make mention of some experiments on the action between copper and distilled water containing air. A piece of sheet-copper (400 cm<sup>2</sup> surface) lost only 0.3 mgrm. when exposed in 100 cc. distilled water for twenty-four hours to a current of air, while lead under the same circumstances lost more than 200 mgrms., zinc about 35 mgrms., and tin only traces. Whilst sea-water free from air does not act on copper (Note 98), this metal is readily corroded when immersed in this water in the presence of air, basic carbonate and basic chloride of copper being formed (Note 99). A. Krefing observed the same substances when copper was submitted to the action of a solution of sodium chloride containing air (Note 100).

In the report presented by G. D. Bengough at the annual general meeting of the Institute of Metals, Jan. 18, 1911 (Note 101), a review occurs of the more important technical papers published on the corrosion of copper and brass and of the views of their authors.

His own views of the problems involved are stated subsequently. Thus, for instance, he remarks that the deposit of basic salt on the copper may become rather firmly attached to it under favourable circumstances. As has been suggested by Tilden (Note 102) this deposit may possibly give rise to a galvanic action, thus promoting the solution of copper in the neighbourhood; pitting being the result. Bengough now states that the above salt can only act in this way, if it is a conductor of electricity, and it is therefore necessary to settle this point first. For, if its action as an electro-negative node be proved, it will be worth while trying to destroy the conditions under which this salt is formed.

Again, there are two factors which according to Bengough have not hitherto been sufficiently investigated—1. The influence of the structure of the metal (fine or coarse crystallisation, porosity, laminations, &c.). 2. The influence of small quantities of impurity in solid solution on the solution tendency and the depolarising action of the

metal. At last the outlines are given of a research scheme. This regards especially the corrosion of condenser tubes by sea-water. An apparatus is described in which a set of forty-eight condenser tubes in 3-ft. lengths may be submitted to this water under different circumstances (increasing temperature, acid solutions, external E. M. F. stagnant water, over-heating, action of electro-negative areas, choking by ashes, shells, seaweed, &c.). It may be mentioned here that Bengough's paper is a Report to the Corrosion Committee of the Institute of Metals. The fact that such a Committee has been appointed to undertake investigations (for which funds have been provided) on the subject of corrosion, speaks volumes for their importance.

Finally attention may be drawn to the fact that the corrosion of copper alloys, such as brass, Muntz metal, &c., is perhaps of still greater interest than that of copper. But the length of this report already so far exceeds the desired length that a discussion of the corrosion of these and other alloys must be omitted.

### 15. Conclusions.

1. The principal investigations in the domain of the corrosion of the six metals named in the heading of this report have been summarised and have been contemplated from the same theoretical points of view.

2. It is not possible to predict whether a special kind of drinking water, brought in contact with lead or zinc under certain circumstances, will only dissolve quantities of lead or zinc compounds below a certain limit. In each special case it will be necessary to make a special experiment in which the practical circumstances are imitated as much as possible. As regards tin, there seems to be little danger of considerable corrosion by drinking water.

3. Experiments are desirable regarding the order of the metals with respect to their potentials, when placed in different salt solutions and kinds of water found in nature.

4. It is desirable to investigate how the potential difference between two metals immersed in these solutions changes in the course of time, when air passes through and to trace the chemical processes which take place.

5. It will be of special importance to investigate whether a "protective layer" is generated during the corrosion of a metal and what its composition is.

6. Further experiments on the passivity of the metals named in this report may appear to be of great interest.

I hope soon to be able to make communications about my own experiments on points 3—6.

### Notes.

95. *Ber.*, 1882, xv., 664; 1885, xviii., 1887. On treating copper with a solution of ammonium carbonate, containing air. Traube also observed the formation of hydrogen peroxide (*Ibid.*, 1885, xviii., 1889). This substance was observed by Ernst Cohen (*De Ingenieur*, 1901) during the corrosion of copper by sea water.

96. *Arb. Kais. Gesundh., amte* xxiii., 287, 1906. Compare also the vivifying influence of Cl-ions on passive metals: Sackur, *Zeit. Electrochem.*, 1904, x., 841.

97. *Arb. Kais. Geshundh., amte* viii., 395, 1893. See also Carnelly, *Journ. Chem. Soc.*, 1874, ii., 1.

98. Ernst Cohen, *De Ingenieur*, 1901, 180. In the presence of air free from carbon dioxide he did not observe corrosion. How long the experiment lasted is not mentioned.

99. Ernst Cohen, *loc. cit.*, p. 181.

100. "Om nogle metallers oxydations ved nøytrale saltes medvirken," *Christiansa Vidensk. Selsk. Forhand.*, 1892, No. 16.

101. *Journ. Inst. of Metals*, 1911, v., 28.

102. *Journ. Soc. Chem. Ind.*, 1886, v., 84.

SOME ASPECTS OF INDUSTRIAL CHEMISTRY.\*

By L. H. BAEKELAND, Sc.D.

(Concluded from p. 94).

Good fuel-gas could be manufactured and distributed to the individual household consumer at considerably cheaper rates, if it were not for antiquated municipal specifications, which keep on prescribing photometric tests instead of insisting on standards of fuel value, which makes the cost of production unnecessarily high, and disregards the fact that, for lighting, the Welsbach mantle has rendered obsolete the use of highly carburetted gas as a bare flame. But for those unfortunate specifications, cheap fuel-gas might be produced at some advantageous central point, where very cheap coal is available; such heating gas could be distributed to every house and every factory, where it could be used cleanly and advantageously, like natural gas, doing away at once with the black coal smoke nuisance, which now practically compels a city like New York to use nothing but the more expensive grades of anthracite coal. It would eliminate, at the same time, all the bother and expense caused through the clumsy and expensive methods of transportation and handling of coal and ashes; it would relieve us from many unnecessary middlemen which now exist between coal and its final consumer.

The newer large-sized internal combustion engines are introducing increasing opportunities for new centres of power production where waste gas of blast-furnaces or coke-ovens, or where deposits of inferior coal or peat are available.

If such centres are situated near tidewater, this may render them still more advantageous for some electrochemical industries, which, until now, were compelled to locate near some inland water-powers.

Nor should we overlook the fact that the newer methods for the production of cheap fuel-gas offer excellent opportunities for an increased production of valuable tar by-products, and more particularly of ammonium salts; the latter would help to a not inconsiderable extent in furnishing more nitrogen fertiliser.

It is somewhat remarkable that a greater effort has already been made to start the industrial synthesis of nitrogen products than to economise all these hitherto wasted sources of ammonia.

In fact, science indicates still other ways, somewhat of a more radical nature, for correcting the nitrogen deficiencies in relation to our food supply.

Indeed, if we will look at this matter from a much broader standpoint, we may find that, after all, the shortage of nitrogen in the world is attributable, to a large extent, to our rather one-sided system of agriculture. We do not sufficiently take advantage of the fact that certain plants, for instance those of the group of Leguminosæ, have the valuable property of easily assimilating nitrogen from the air, without the necessity of nitrogen fertilisers. In this way the culture of certain Leguminosæ can insure enough nitrogen for the soil, so that in rotation with nitrogen consuming crops, like wheat, we could dispense with the necessity of supplying any artificial nitrogen fertilisers.

The present nitrogen deficiency is influenced further by two other causes—

The first cause is our unnecessarily exaggerated meat diet, in which we try to find our proteid requirements, and which compels us to raise so many cattle, while the amount of land which feeds one head of cattle could furnish, if properly cultivated, abundant vegetable food for a family of five.

The second cause is our insufficient knowledge of the way to grow and prepare for human food just those vegetables which are richest in proteids. Unfortunately, it so happens that exactly such plants as, for instance, the soy-bean are not by any means easily rendered palatable and

digestible, while any savage can eat raw meat, or can readily cook, boil, or roast it for consumption.

On this subject we can learn much from some Eastern people, like the Japanese, who have become experts in the art of preparing a variety of agreeable food products from that refractory soy-bean, which contains such an astonishingly large amount of nutritious proteids, and which, long ago, became for Japan a wholesome, staple article of diet.

But, on this subject, the Western races have not yet progressed much beyond the point of preparing cattle-feed and paint oil from the soy-bean, although the more extended culture of this, or similar plants, might work about a revolution in our agricultural economics.

Agriculture, after all, is nothing but a very important branch of industrial chemistry, although most people seem to ignore the fact that the whole prosperity of agriculture is based on the success of that photochemical reaction which, under the influence of the light of the sun, causes the carbon dioxide of the air to be assimilated by the chlorophyll of the plant.

It is not impossible that photochemistry, which hitherto has busied itself, almost exclusively, within the narrow limits of the art of making photographic images, will, some day, attain a development of usefulness at least as important as all other branches of physical chemistry. In this broader sense, photochemistry seems an inviting subject for the agricultural chemist. The possible rewards in store in this almost virgin field may, in their turn, by that effect of superinduction between industry and science, bring about a rapid development similar to what we have witnessed in the advancement of electricity, as well as chemistry, which both began to progress by bounds and leaps, way ahead of other sciences, as soon as their growing industrial applications put a high premium on further research.

Photochemistry may allow us some day to obtain chemical effects hitherto undreamed of. In general, the action of light in chemical reactions seems incomparably less brutal than all means used heretofore in chemistry. This is the probable secret of the subtle chemical syntheses which happen in plant life. To try to duplicate these delicate reactions of nature by our present methods of high temperatures, electrolysis, strong chemicals, and other similar torture-processes, seems like trying to imitate a masterpiece of Gounod by exploding a dynamite cartridge between the strings of a piano.

But there are endless other directions for scientific research, relating to industrial applications, which, until now, do not seem to have received sufficient attention.

For instance, from a chemical standpoint, the richest chemical enterprise of the United States, the petroleum industry, has hitherto chiefly busied itself with a rather primitive treatment of this valuable raw material, and little or no attention has been paid to any methods for transforming at least a part of these hydrocarbons into more ennobled products of commerce than mere fuel or illuminants.

A hint as to the enormous possibilities which may be in store in that direction is suggested by the recent work in Germany and England on synthetic rubber; the only factor which prevents extending the laboratory synthesis of rubber into an immense industrial undertaking, is that we have not yet learned how to make cheaply the isoprene or other similar non-saturated hydrocarbons which are the starting point in the process which changes their molecules, by polymerisation, into rubber.

Nor has our science begun to find the best uses for such inexpensive and never exhaustible vegetable products as cellulose or starch. Quite true, several important manufactures, like that of paper, nitrocellulose, glucose, alcohol, vinegar, and some others, have been built on it; but to the chemist at least it seems as if a much greater development is possible in the cheaper and more extended production of artificial fibre. Although we have succeeded in making so-called artificial silk, this article is

\* The Chandler Lecture, Columbia U S A., 1914.

still very expensive; furthermore, we have not yet produced a cheap, good, artificial fibre of the quality of wool.

If we have made ourselves independent of Chile for our nitrogen supply, we are still absolutely at the mercy of the Stassfurt mines in Germany for our requirements of soluble potash-salts, which are just as necessary for agriculture. Shall we succeed in utilising some of the proposed methods for converting that abundant supply of feldspar, or other insoluble potash-bearing rocks, into soluble potash-salts by combining the expensive heat treatment with the production of another material like cement, which would render the cost of fuel less exorbitant? Or shall the problem be solved in setting free soluble potassium salts as a by-product in a reaction engendering other staple products consumed in large quantities?

We have several astonishingly conflicting theories about the constitution of the centre of the globe, but we have not yet developed the means to penetrate the world's crust beyond some deep mines—merely an imperceptible faint scratch on the surface—and in the meantime, we keep on guessing, while to-day astronomers know already more about the surface of the planet Mars than we know about the interior of the globe on which we live.

Nor have we learned to develop or utilise the tremendous pressures under which most minerals have been formed, and still less do we possess the means to try these pressures, in conjunction with intensely high temperatures.

No end of work is in store for the research chemist, as well as for the chemical engineer, who can think by himself, without always following the beaten track. We are only at the beginning of our successes, and yet, when we stop to look back to see what has been accomplished during the last generations, that big jump from the rule-of-thumb to applied science is nothing short of marvellous.

Whoever is acquainted with the condition of human thought to-day must find it strange, after all, that scarcely seventy years ago, Mayer met with derision even amongst the scientists of the time, when he announced to the world that simple but fundamental principle of the conservation of energy.

We can hardly conceive that just about the time the Columbia School of Mines was founded, Liebig was still ridiculing Pasteur's ideas on the intervention of micro-organisms in fermentation which have proved so fecund in the most epoch-making applications in science, medicine, surgery, and sanitation, as well as in many industries.

Fortunately, true science, contrary to other human avocations, recognises nobody as an "authority," and is willing to change her beliefs as often as better studied facts warrant it; this difference has been the most vital cause of her never ceasing progress.

To the younger generation, surrounded with research laboratories everywhere, it may cause astonishment to learn that scarcely fifty years ago, that great benefactor of humanity, Pasteur, was still repeating his pathetic pleadings with the French government to give him more suitable quarters than a damp, poorly lighted basement, in which he was compelled to carry on his research; and this was, then, the condition of affairs of no less a place than Paris, the same Paris that was spending, just at that time, endless millions for the building of her new Opera Palace.

Such facts should not be overlooked by those who might think that America has been too slow in fostering chemical research.

If the United States has not participated as early as some European countries in the development of industrial chemistry, this was chiefly because conditions here were so totally different from those of nations of Germany, England, and France, that they did not warrant any such premature efforts.

In a country as full of primary resources, agriculture,

forests, mines, and the more elementary industries directly connected therewith, as well as the problems of transportation, appealed more urgently to American intellectual men of enterprise.

Why should anybody here have tried to introduce new difficult or risky chemical industries, when on every side more urgently important fields of enterprise were inviting all men of initiative?

Chemical industries develop along the lines furnished by the most immediate needs of a country. Our sulphuric acid industry, which can boast to-day of a yearly production of about three million tons, had to begin in an exceedingly humble way, and the first small amounts of sulphuric acid manufactured here found a very scant outlet.

It required the growth of such fields of application as petroleum refining, superphosphates, explosives, and others, before the sulphuric acid industry could grow to what it is to-day.

At present similar influences are still dominating our chemical industries; they are generally directed to the mass production of partly manufactured articles. This allows us to export at present to Germany chemicals in crude form, but in greater value than the total sum of all the chemical products we are importing from her; although it cannot be denied that a considerable part of our imports are products like alizarin, indigo, aniline dyes, and similar synthetic products which require higher chemical manufacturing skill.

In this connection it may be pointed out that our exports of oleomargarine, to Germany alone, are about equivalent to our imports of aniline dyes.

But all this does not alter the fact that in several important chemical industries the United States has been a pioneer. Such flourishing enterprises as that of the artificial abrasives, carborundum and alundum, calcium carbide, aluminium, and many others, testify how soon we have learned to avail ourselves of some of our water-power.

One of the most important chemical industries of the world, the sulphite cellulose industry, of which the total annual production amounts to three and a-half million tons, was originated and developed by a chemist in Philadelphia, B. C. Tilgman. But its further development was stopped for awhile on account of the same old trouble, lack of funds, after 40,000 dolrs. were spent, until some years later it was taken up again in Europe and reintroduced in the United States, where it has developed to an annual production of over a million tons.

What has been accomplished in America in chemical enterprises, and what is going on now in industrial research, has been brilliantly set forth by Mr. Arthur D. Little (*Journ. of In. and En. Chem.*, October, 1913, vol. 5, No. 10).

Nor at any time in the history of the United States was chemistry neglected in this country; this has recently been brought to light in the most convincing manner by Professor Edgar F. Smith of Philadelphia ("Chemistry in America," published by D. Appleton and Co., New York and London, 1914).

The altruistic fervour of that little group of earlier American chemists who, in 1792, founded the Chemical Society of Philadelphia (probably the very first chemical society in the world), and in 1811, the Columbia Chemical Society of Philadelphia, is best illustrated by an extract of one of the addresses read at their meeting in 1798:—

"The only true basis on which the independence of our country can rest are agriculture and manufactures. To the promotion of these nothing tends in a higher degree than chemistry. It is this science which teaches man how to correct the bad qualities of the land he cultivates by a proper application of the various species of manure, and it is by means of a knowledge of this science that he is enabled to pursue the metals through the various forms they put on in the earth, separate them from substances which render them useless, and at length manufacture them into

the various forms for use and ornament in which we see them. If such are the effects of chemistry, how much should the wish for its promotion be excited in the breast of every American! It is to a general diffusion of knowledge of this science, next to the virtue of our countrymen, that we are to look for the firm establishment of our independence. And may your endeavours, gentlemen, in this cause, entitle you to the gratitude of your fellow-citizens."

This early scientific spirit has been kept alive throughout the following century by such American chemists as Robert Hare, E. N. Horsford, Wolcott Gibbs, Sterry Hunt, Lawrence Smith, Carey Lea, Josiah P. Cooke, John W. Draper, Willard Gibbs, and many others still living.

Present conditions in America can be measured by the fact that the American Chemical Society alone has over seven thousand members, and the Chemists' Club of New York has more than a thousand members, without counting the more specialised chemical organisations, equally active, like the American Institute of Chemical Engineers, the American Electrochemical Society, and many others.

During the later years, chemical research is going on with increasing vigour, more especially in relation to chemical problems presented by enterprises which at first sight seem rather remote from the so-called chemical industry.

But the most striking symptom of newer times is that some wealthy men of America are rivalling each other in the endowment of scientific research on a scale never undertaken before, and that the scientific departments of our Government are enlarging their scope of usefulness at a rapid rate.

But we are merely at the threshold of that new era where we shall learn better to use exact knowledge and efficiency to bring greater happiness and broader opportunities to all.

However imposing may appear the institutions founded by the Nobels, the Solvays, the Mondes, the Carnegies, the Rockefellers, and others, each of them is only a puny effort to what is bound to come when governments will do their full share. Fancy that if, for instance, the Rockefeller Institute is spending to good advantage about half a million dollars per annum for medical research, the chewing-gum bill of the United States alone would easily support half-a-dozen Rockefeller Institutes; and what a mere insignificant little trickle all these research funds amount to, if we have the courage to compare them to that powerful gushing stream of money which yearly drains the war budget of all nations.

In the meantime, the man of science is patient and continues his work steadily, if somewhat slowly, with the means hitherto at his disposal. His patience is inspired by the thought that he is not working for to-day but for to-morrow. He is well aware that he is still surrounded by too many "men of yesterday," who delay the results of his work.

Sometimes, however, he may feel discouraged that the very efficiency he has succeeded in reaching at the cost of so many painstaking efforts, in the economical production of such an article of endlessly possible uses as Portland Cement, is hopelessly lost many times over and over again by the inefficiency, waste, and graft of middlemen and political contractors, by the time it gets on our public roads or in our public buildings. Sometimes the chaos of ignorant brutal waste which surrounds him everywhere may try his patience. Then again, he has a vision that he is planting a tree which will blossom for his children and will bear fruit for his grandchildren.

In the meantime, industrial chemistry, like all other applications of science, has gradually called into the world an increasing number of men of newer tendencies, men who bear in mind the future rather than the past, who have acquired the habit of thinking by well-established facts instead of by words, of aiming at efficiency instead

of striking haphazard at ill-defined purposes. Our various engineering schools, our universities, are turning them out in ever increasing numbers, and better and better prepared for their work. Their very training has fitted them out to become the most broad-minded progressive citizens.

However, their sphere of action, until now, seldom goes beyond that of private technical enterprises for private gain. And yet, there is not a chemist, not an engineer, worthy of the name, who would not prefer efficient, honourable public service, freed from party politics, to a mere money-making job.

But most governments of the world have been run for so long almost exclusively by lawyer-politicians that we have come to consider this an unavoidable evil, until sometimes a large experiment of government by engineers, like the Panama Canal, opens our eyes to the fact that, after all, successful government is—first and last—a matter of efficiency, according to the principles of applied science.

Was it not one of our very earliest American chemists, Benjamin Thompson, of Massachusetts, later knighted in Europe as Count Rumford, who put in shape the rather entangled administration of Bavaria by introducing scientific methods of government?

Pasteur was right when one day, exasperated by the politicians who were running his beloved France to ruin, he exclaimed—

"In our century, science is the soul of the prosperity of nations and the living source of all progress. Undoubtedly, the tiring daily discussions of politics seem to be our guide. Empty appearances!—What really leads us forward are a few scientific discoveries and their applications."

#### EXPANSION OF CHEMICAL AND DYE-STUFF INDUSTRY IN UNITED STATES.\*

On October 15 a Committee was appointed by the Chairman of the New York Section of the American Chemical Society to investigate into the feasibility of expanding the chemical and dye-stuff industry in the United States. This Committee consisted of Bernhard C. Hesse, Chairman, L. B. F. Herreshoff, H. A. Metz, I. F. Stone, D. W. Jayne, J. Merritt Matthews, and Allen Rogers. On November 6 the Committee submitted its report together with its recommendations. This report, with the exception of the introductory paragraphs, was as follows:—

Your Committee has carefully considered all the public suggestions as to methods of improvement, and has searched through the governmental regulations of the belligerent nations as to embargo, and as to contraband of war, in order to construct therefrom a list of chemicals, inclusive of dye-stuffs, which have thereby been shut off from the United States, in the hope of thus being placed in a position to make specific recommendations of value.

It can be fairly stated that, in general, the chemical industry of this country is efficiently exploited, and is making full use of all the opportunities presented to it under the normal conditions existing prior to the state of hostilities. Some of the chemicals which are imported from abroad are made in considerable amounts in this country as well, and the amount imported under normal conditions depends upon the ordinary normal fluctuations of business conditions both here and abroad. With the stoppage of this foreign supply the domestic production was not at once capable of making up the deficiency, but in a number of instances the American manufacturers have taken steps to increase their capacity, and the strain in the market of those particular things will exist no longer than it will require to extend the manufacturing facilities to the proper extent.

\* From the *Chemical Engineer*, xx., No. 6.

Among these are ammonia salts, barium chloride, barium nitrate, bleaching powder, sodium cyanide, yellow prussiate, sodium nitrate, sodium hydrosulphite, zinc dust.

If, however, it be desired and if public necessity requires the introduction of the manufacture of explosives and further chemicals and dye-stuffs into our home industry, such as coal-tar product explosives, pharmaceuticals, medicinals, and other intermediates and finished coal-tar dyes, then alterations of our tariff law are inevitable, and the consumers in the first place and the public in general must share in the burden thus imposed. If conditions of national defence in case of attack by a foreign power require us to manufacture our own explosives, and to be in that regard independent of all foreign nations at all times, or if our textile industries or any other of our industries requiring coal-tar chemicals, such as dye-stuffs, shall for ever be protected and made independent of foreign nations for the supply of those materials, then the nation as a whole must bear the burden incident to such expansion. Under existing circumstances private enterprise and private capital have gone their limit. They have reached the limit for two reasons:—

1. The explosive, dye, and similar industries abroad, just referred to, are in a state of high development and of refined organisation, and are financially the best suited to carry on an offensive campaign against any nation attempting to take business away from them.

2. Domestic manufacturers are prohibited by law from making use of co-operative commercial devices, such as pools, trusts, manufacturing and selling agreements, and the like, whereas such devices are wholly lawful abroad, and are encouraged by the respective governments. In other words, the American chemical industry is expected to cope with the foreign industry while both its own arms are tied behind its back, and its opponents have full and free use of their arms.

**Anti-dumping Clause.**—The remedies required would be an effective anti-dumping clause that would certainly prevent underselling of domestic manufactures in the United States by unfair methods. What the form of such clause shall be is a problem with which your Committee is unable to cope; it is strictly a law-making and law-enforcing problem, and is allied to the usual problem of determining under-valuation as heretofore carried on by our Treasury Department; it, however, is a much more refined problem than the older problem of proving under-valuation. Nevertheless, your Committee believes that with such a mechanism in our law that much would be done toward encouraging our chemical industries.

**To Create Coal-tar Chemical Industry.**—According to the best information that your Committee can gather, such an anti-dumping clause alone would not be sufficient, however, to create complete and independent domestic coal-tar explosives, dye-stuffs, and medicinals industries. It has been conclusively demonstrated during the past thirty years that the present tariff rate of 30 per cent on dye-stuffs is not sufficient to induce the domestic dye-stuff industry to expand at a rate comparable with the consumption of dye-stuffs in this country, and that therefore all dye-stuffs made from coal-tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal-tar, should all be assessed alike, namely, 30 per cent *ad valorem* plus 7½ cents per pound specific, and that all manufactured products of or obtainable from coal-tar, themselves not dyes or colours and not medicinal, shall be taxed 15 per cent *ad valorem* and 3½ cents per pound specific.

**Tariff to Aid Dye Industry.**—The best information and judgment your Committee can obtain is that the above manufactured products of coal-tar, not dyes and not colours and not medicinal, should carry one-half the duty of the finished coal-tar dye, and that the above rate of 30 per cent *ad valorem* and 7½ cents specific would probably be sufficient to encourage and enable domestic manufacturers

to expand their operations to such an extent as to supply a very material increase in, if not the whole, of these commodities consumed in this country. The reason for a specific duty is to protect the domestic manufacturer in the manufacture of the relatively cheap dyes, such as the cheap scarlets, the cheap yellows, and the like, whose prices abroad are in the neighbourhood of from 12 cents to 20 cents per pound, with dyes of that type 30 per cent *ad valorem* would not offer so serious an obstacle to importation and underselling thereof as does the 7½ cents per pound specific; on the other hand, on dyes whose prices are 1 dol. and upward per pound the function of the 7½ cents specific more nearly approaches zero. That is, with the cheap dyes the chief function lies in the specific portion of the duty, and with the expensive dyes the chief function lies with the *ad valorem* portion of the duty.

This is said to be the price the nation will have to pay to have a complete self-contained and independent coal-tar chemical industry. However, it must be remembered that if such an industry be created and importation of coal-tar products, inclusive of intermediates and dyes, is restricted its ultimate effect upon the Federal revenues will have to be considered. It will therefore be necessary to determine carefully if the advantages to be gained are equal to the price to be paid.

**Patent Laws.**—This Committee is a unit in the belief that an alteration of our patent laws aiming at compulsory working or compulsory licensing would not be any substantial benefit to this industry or to the country as a whole. Twenty-nine countries have attempted compulsory licensing clauses and fifty-six countries have attempted compulsory working clauses, and the best information your Committee can obtain is that in none of these attempts has there been any appreciable measure of success. While it may be true that under extraordinary conditions, such as now exist, compulsory licensing might have some advantage, yet it is equally true that in normal times the disadvantage due to compulsory licensing or compulsory working would more than overbalance any advantage at all likely to be obtained under stress of unusual conditions.

In none of the countries where there have been working or licensing clauses, or both, co-extensive with the existence of the coal-tar chemical industry, has there been established any real coal-tar chemical industry, and your Committee does not feel that an alteration in our present patent laws could be made which would be effective against foreigners, and at the same time not be onerous and a hardship to domestic inventors. Your Committee believes that in the long run and in the final outcome, our present system with regard to working and licensing is as efficient as that of any other country. In the dye-stuffs industry in particular there are so many non-patented commercial products and so many commercial products once patented now free from patent restraint that their production alone would form a basis for a very considerable industry, and your Committee feels that the way to encourage that industry, if the establishment of that industry in this country be a national necessity, is through a change in the tariff and the additional anti-dumping feature in the administration of the tariff, and not through any change in the patent laws. Once established, such an industry could develop and ultimately cope with any foreign combination upon fair and equal terms. Over 60 per cent of the tonnage and of the individual dyes used in the United States will be free from any patent restraint within the next four years; over 75 per cent of the dyes are now in that condition.

**Availability of Raw Materials.**—The best information your Committee has so far been able to gather is that this country can produce so called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry, inclusive of explosives and dyes, provided there is a certainty of outlet as to volume and continuity. Those engaged in manufacture here do not want to expand unless the dye-users are willing to



make corresponding contracts. In other words, it is a close circle. If the dye-users will contract sufficiently with the dye-makers, the dye-makers will contract with the coal-tar distillers, and the industry will take a start. The initiative rests wholly with the users; if they cannot afford to contract the dye-maker and the distillers cannot afford to make their contracts and additional investments.

(To be continued).

## INSTITUTE OF INDUSTRY AND SCIENCE.

It is officially announced that, in view of important developments, the Institute of Industry and Commerce have now changed their name to that of "Institute of Industry and Science of Great Britain and Ireland." The word "Commerce" has been dropped in order not to confuse the Institute with other existing associations, and also to more clearly define the objects of the Institute in its title.

Considerable support is being extended to the Institute by the leaders of industry and science and many of the important trade organisations.

The Institute of Industry and Science is a counterpart of a German organisation known as the Hansa Bund, which is in reality a Chamber of Manufacturers', Shippers', and Trade Organisations, *s.e.*, a confederation of important German firms for promoting, encouraging, and facilitating German industry, commerce, and expansion of foreign trade. The advantage which the Institute of Industry and Science has is that it is non-political, whereas the Hansa Bund is of a somewhat political character, inasmuch as it may be said to be attached to the German Liberal Parliamentary Party, as opposed to the Junker policy.

The Hansa Bund was founded in 1909, and has its head office in Berlin, with a large branch at Hamburg, and has a comprehensive membership. It holds meetings and publishes papers and reports upon all matters relating to the welfare of German industry and finance. The present German Minister of Finance was an active member of the Bund.

The Institute of Industry and Science is founded on somewhat superior lines, suited to British conditions, and it is non-political in character. The Court of Directors hope, therefore, that all who are interested in the development of British industry with the aid of science and scientific methods, will actively support the Institute and become members. The Directors propose to devote a proportion of its revenue each year to scientific research work, under the supervision of the most eminent men of science, as set forth in the objects of the Institute.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 11, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Lepidostrobos kentuckiensis*, *nomen nov.*, formerly *Lepidostrobos Fischeri*, Scott and Jeffrey." (A Correction). By Dr. D. H. SCOTT, For. Sec. R.S.

"*The Excitatory Process in the Dog's Heart*. Part II. *The Ventricles*." By T. LEWIS and M. A. ROTHSCHILD.

"*Variation in the Growth of Mammalian Tissue in vitro according to the Age of the Animal*." By A. J. WALTON.

## INDIAN SCIENCE CONGRESS.

(CHEMISTRY SECTION).

THE meeting of the Chemistry Section of the Second Indian Science Congress was held in the Presidency College, Madras, on Friday, January 15, at 10 a.m., and was well attended. On the whole the meeting was distinctly encouraging; it showed that a fair amount of research is being carried out in various parts of India, and that this is not confined to Europeans.

The Chairman, Prof. P. C. RAY, C.I.E., of Calcutta, read two papers—"Tautomeric Changes in Organic Thiocompounds through the Agency of Mercuric Nitrite, Heavy Metallic Chlorides, and Monochloroacetic Acid," and "The Interaction of Dimercuriammonium Nitrite and Ethyl Iodide." The results communicated were distinctly interesting, but as the work has not been completed there could be little discussion.

Prof. J. J. SUBBOROUGH, of Bangalore, described work which has been carried out under his direction by his students at the Indian Institute of Science. In the first paper, "*Studies in Alcohololysis*," he was able to show the almost complete analogy between the transformation of esters and esterification, and in the second paper, "*Replacement of Sulphonic Acid Groups*," he gave an account of the action of halogens on various sulphonic acids, which result in the replacement of the acid group.

Prof. NEOGI, of Rajshahi, read an account of his work on the conversion of aliphatic nitrites into nitrocompounds and the reduction of aliphatic nitrites to amines.

Prof. A. F. JOSEPH, of Colombo, described the careful work which he had done in conjunction with Mr. W. N. RAO on the chemistry of chromium phosphate.

Dr. H. E. WATSON, of Bangalore, showed a diagram and illustrated the working of an ingenious and elaborate apparatus for determining the compressibility of gases at low temperatures.

Profs. C. S. GIBSON and J. L. SIMONSEN described the resolution of externally compensated alanine derivatives and of reduced naphthoquinolindines by various methods into their optically active components, while Prof. Simonsen also communicated results of experiments, in which he had been partly assisted by one of his students, on the nitration of 3-acetyl amino 2-methoxy toluene and on condensations with monochloromethyl ether.

The above brief account of some of the papers read at the meeting shows that the research work in pure chemistry in India is of a varied character, and attains a high standard. It is hoped that the Annual Meetings of the Science Congress will do much to encourage further activity on the part of Indians in this field, and that in the various university colleges will be given increased facilities for scientific investigations.

## NOTICES OF BOOKS.

*Directions for a Practical Course in Chemical Physiology.* By W. CRAMER, Ph.D., D.Sc. Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THIS book contains an exceedingly useful course of practical work in chemical physiology for medical students, and it is not at all surprising that a new edition has been called for very soon after the issue of the first. The arrangement of the work is distinctly novel, the early experiments being comparatively simple, and dealing with familiar substances, such as the potato, eggs, lard, butter, &c., from which the proximate constituents are prepared, and their chemical reactions and physical properties studied. The way is thus satisfactorily paved for more difficult work. In the second edition the use of the polarimeter is well described, and some new and valuable experiments on the coagulation of the blood are introduced.

**Bonecourt Patent Waste Heat Boilers and Water Heaters.**  
Westminster: Bonecourt Waste Heat Boiler Co., Ltd.

In the Bonecourt Patent Waste Heat Boilers and Water Heaters use is made in the most efficient and effective manner of the heat discharged in the exhaust gases of internal combustion engines. The manufacturers claim that the boiler is an effective silencer, requires absolutely no attention, and is easy and cheap to instal. It can be used either for providing additional steam power or for a continuous supply of hot water, and many different forms are described and illustrated in the pamphlet.

**Le Rotazioni Ionomagnetiche. ("Ionomagnetic Rotation").**  
By AUGUSTO RIGHI. Bologna: Nicolo Zanichelli.

This book contains the text of a lecture which was delivered by the author before the Italian Electrotechnical Association at the conference of the Society held at Bologna in November, 1914. Some additions have been made to throw further light upon the phenomena described, and bibliographical references are included. A clear account is first given of the electron theory and the electrical theory of matter, and the author's own valuable researches on ionomagnetic rotation and the explanation he gives of the new phenomenon are fully discussed. The pamphlet should be read by all who are interested in modern physical research.

## CORRESPONDENCE.

### SCIENCE AND THE STATE.

To the Editor of the Chemical News.

SIR,—Very shortly before the outbreak of war a newspaper correspondence, in which many writers took part, seemed to point to the conclusion as accepted that in this country the utilisation of scientific method and the status to be accorded to scientific men had not hitherto been properly appreciated by the Government or the public. Since the commencement of the war public opinion seems to have adopted and emphasised this view, at least so far as the utterances of public men, officials, and newspaper correspondents may be taken as evidence. The following advertisement from the columns of the CHEMICAL NEWS shows the sort of figure at which Government departments value scientific assistance at the present time:—

#### INSPECTION DEPARTMENT.

#### ROYAL ARSENAL, WOOLWICH,

Wanted immediately, Temporary Assistant Chemists.

Applicants must have had a thorough training in Inorganic and Organic Chemistry, and must be accurate Analysts. University Graduates or Members of the Institute of Chemistry will have preference.

Wages £2 os. 6d. per week.

Applications, giving particulars of training and experience, and accompanied by copies of not more than three recent testimonials should be addressed to CHIEF INSPECTOR, Royal Arsenal, Woolwich.

Does Chief Inspector seriously think that a trained chemist is worth no more than the "wages" he offers, which are subject to the deduction of 4d. per week for insurance?

Does he realise that the kind of man he is asking for has in all cases spent at least five or six years in acquiring his technical skill, and during that time has provided maintenance and fees at his own cost?

I am informed that these assistant chemists have been wanted for the past three or four weeks, but that no applicants for the post have appeared; hence the advertisement.

If any applicants do turn up it is certain that, like all other scientific men of British birth, they are animated by the patriotic desire to be useful to their country, and are willing to disregard official insolence. But it will have to be remembered that, when the war is over, the Government of this country will not continue to receive scientific

assistance at the wages of unskilled labour, alongside of which it is now ranked.

For my part, I hope that no response will be made to this advertisement, for it is now more than ever necessary that the public should be lifted out of its state of ignorance as to the training, qualifications, and functions of chemists.—I am, &c.,

WILLIAM A. TILDEN.

The Oaks, Northwood, Middlesex,  
February 15, 1915.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 3, January 18, 1915.

**Tautomerism of Phenylpyruvic Acid.**—J. Bougaud and R. Hemmerlé.—Phenylpyruvic acid can exist in the enol and ketonic forms. When the former is saturated with potassium bicarbonate or acetate it is gradually converted into the ketone form. The sodium salt of the ketone form when acidulated with hydrochloric acid gives a precipitate of the enol form. These transformations are accelerated by raising the temperature. The alkalis, like acids, are capable of converting the ketone into the enol form. By boiling phenylpyruvic acid with acetic anhydride

$$\text{C}_6\text{H}_5\cdot\text{CH}=\text{C}\cdot\text{CO}_2\text{H}$$
an acetate of formula 
$$\text{C}_6\text{H}_5\cdot\text{CH}=\text{C}\cdot\text{CO}_2\text{CH}_3$$
 is formed.

## MEETINGS FOR THE WEEK.

MONDAY, March 1st.—Royal Society of Arts, 8 (Fothergill Lecture).

— "Motor Fuels," by Prof. V. B. Lewis.

TUESDAY, 2nd.—Royal Institution, 3 General Meeting.

— "Colour Photography: Scientific Applications," by Prof. W. J. Pope F.R.S.

— Royal Society of Arts, 4.30. "The Northern Territory of Australia: Past, Present, and Future," by D. Lindsay.

WEDNESDAY, 3rd.—Royal Society of Arts, 4.30. "Shakespeare's Profession" by W. Poel.

— Society of Public Analysts, 6. "Soluble Chlorides, and Total Chlorine in some English Cakes," by S. W. Bridge. "Routine Detection and Estimation of Boric Acid in Butter," by H. Hawley. "Structure of Pepper: some New Features," by T. E. Wallis. "Occurrence of Chlorine in Coal," by A. de Waele.

THURSDAY, 4th.—Royal Institution, 3. "Poetry and War," by Sir Herbert Warren, K.C.V.O.

— Royal Society. "A Volumetric Method of Determining the Efficiency of Radiating Bodies," by W. A. Bone, H. L. Callendar, and H. J. Yate. "Simplification of the Arithmetical Processes of Evolution and Revolution," by R. Chappell. "Elastic Properties of Steel at Moderately High Temperatures," by J. E. Rowatt. "Steric Influence, Static and Dynamic," by O. C. M. Davis and F. W. Rixon. "Interaction of Dimercuriammonium Nitrate and the Alkali Iodides—Nascent Mercurous Nitrate," P. C. Ray. "Constitution of Allantoin and Allied Substances," by H. D. Dakin.

FRIDAY, 5th.—Royal Institution, 9. "Mimicry and Butterflies," by Prof. E. B. Poulton.

SATURDAY, 6th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

**Royal Institution.**—On Tuesday next, March 2, at 3 o'clock, Prof. W. J. Pope will begin a course of two lectures at the Royal Institution on "Colour Photography—Scientific Applications": (1) "Photographic Appreciation of Colour in Monochrome"; (2) "Photography in Natural Colours." On Thursday, March 4, Sir Herbert Warren begins a course of two lectures on "Poetry and War." The Friday Evening Discourse on March 5 will be delivered by Prof. E. B. Poulton on "Mimicry and Butterflies"; and on March 12 by Sir Rickman J. Godlee, on "Back to Lister."

# THE CHEMICAL NEWS.

Vol. CXI., No. 2884.

## BRITISH IMPERIALISM. GERMAN KULTUR DEFINED.\*

By J TAYLOR PEDDIE, F.S.C

In any consideration which is given to the working conditions which govern our national welfare we must not lose sight of the fact that as the leader of the greatest empire the world has known we have to assume great responsibilities to the constituent parts of the Empire, and to the world at large. Whether we do so adequately is another matter, but the fact remains that men, after their primary wants are satisfied, seek for higher culture. It is this aspect of human activity which keeps the world moving and is the embodiment of the Christian doctrine. Certain it is that without the will to live for a definite objective life would cease to have any attraction for individuals. Goethe admirably expresses it in the following lines:—

"He only gains his freedom and existence  
Who daily conquers them anew."

Leaders of German thought have long since recognised this aspect of human existence, and have developed ideals now known to us as "German Kultur." These ideals are roughly as follows:—

1. The equalisation of all opportunities for the individuals in the State.
2. The preparation and development of individuals, through education and science, for the duties which lie before them as citizens of the State.
3. That the duties which such individuals shall render to the State shall be more efficiently performed than the duties which the citizens of other nations may render to their respective States.
4. That the various forces which constitute the life of the State, such as politics, the army, navy, industry, science, and education, shall be organised in their respective spheres of activity and work cohesively for the national purpose.

The question we have to solve is whether these German ideals have been established upon principles which in all of their essentials are sound from the democratic and Christian point of view; we think they have. But the rocks upon which these ideals have been broken, for the present, are feudalism, absolute monarchism, and militarism. The absolute monarch, *i.e.*, the Kaiser, has made the ideals subservient to his own purpose, and, taken as a whole, from the Kaiser's standpoint, we find a revival of an old economic principle.

If we examine our history we will find that no large or varied economic activity has been possible under the ascendancy of feudalism or absolute monarchism. Whilst feudalism and absolute monarchism may have been indispensable in the days when men were not as intelligent or educated as they are to-day, for the preservation of order and public defence, it is certainly out of place in this age of democracy. In the days of Plato we find that the governing factor in the life of the State was then, in an extreme form, the subordination of the individual to the will of the State. Among the ruling classes there was a contempt for those citizens who were engaged in industrial occupations. Every form of production, with a partial exception in favour of agriculture, was branded as unworthy of a free man; the only noble forms of activity were considered to be those directly connected with public life, whether military or administrative, and even Plato was

impressed with the advantage of specialisation and organisation in the life of the State. He explains clearly how the different wants and capacities of individuals demand and give rise to mutual services, and how, by the restriction of each to the sort of occupation to which, by his position, abilities, and training, he is best adapted, everything needful for the whole is more easily and better produced or effected.

These views held sway until we reach Aristotle, and we find this great thinker modifying the views held by Plato. Aristotle traced the origin of society not to economic necessities, but to the natural social impulses in the human constitution, the nature of the social union when thus established being determined by the partly spontaneous, partly systematic, combination of diverse activities; and he respects the independence of the latter whilst seeking to effect their convergence. On these grounds he opposes himself to the suppression of personal freedom and initiative, and the excessive subordination of the individual to the State. Aristotle summarily rejects many of the other theories held by Plato, but the point we desire to emphasise is this, that German Kultur, in principle, was advocated by Plato for precisely the same purpose as the Kaiser and other rulers of Germany had in view prior to the declaration of war. Aristotle seems to have been more democratic in his sympathies except in so far that he advocated the exclusion from any share in the government of the State the immediate cultivators of the soil, the artificers, and mechanics, as he held the view that they were apt to be debased by the nature of their occupations. These views no doubt conform to those held by the advocates of German militarism.

We have now shown that "German Kultur" as exemplified in the Kaiser and his military school is nothing new, but is a glorified expression of the views held by the ancients. The subtle feature of the new Kultur, however, is in the higher intellectual development of the citizens of the German State through education and science in order that they shall

- (a) The more efficiently sustain the army and navy out of the profits of industry;
- (b) As members of the army and navy provide more efficient cannon fodder and be able to conduct the great War on scientific principles.

Whilst, therefore, we may condemn "German Kultur" as exemplified by the military school in Germany, let us examine the reason of the successful accomplishment of the objective the Kaiser and his military school have had in view. We do not have to go far for the solution, and it is this: If we exclude militarism and all it stands for from what is known as "German Kultur" we have a set of ideals remaining which have a vital, sustaining, and elevating influence. In the words of Professor Cramb, Germany may or may not attain the world empire of which she dreams; but in the race for the spirit's dominion, the mightier empire of human thought, who is her rival? Where even is her competitor? Not England assuredly; for in that region England in the twentieth century has a place retrograde almost as Austria or Spain.

We are not inclined to be as pessimistic as to the future as Professor Cramb, for we have the capacity to equal the German standard if we will but organise. The want of result is simply due to want of organisation. Our leading men of science, education, and industry are as great as those of Germany, but we have, as a nation, not been educated to appreciate the significance of the words co-ordination, cohesion, and organisation. The errors of the German system can be avoided so long as we do not subject any organisation that may be deemed desirable to the will of the state. It must be based on freedom and the retention of the right of initiation.

Whilst we may destroy Germany as a military power yet we can never destroy her power as an intellectual nation, for her methods of organisation ensure continuity of policy and quality. And this brings us to the point

\* Read at the Institute of Industry and Science.

where we must ask ourselves what have we to offer in this sphere of activity as the leaders in the greatest Empire of the world.

Professor Cramb defines the aim of British imperialism as follows: To give all men within its bounds an English mind; to give all who come within its sway the power to look at the things of man's life, at the past, at the future, from the standpoint of an Englishman; to diffuse within its bounds that high tolerance in religion which has marked this Empire from its foundation; that reverence yet boldness before the mysteriousness of life and death characteristic of our great poets and our great thinkers; that higher justice and a larger freedom which, rightly or wrongly, we associate with the temper and character of our race wherever it is dominant and secure.

But are these political ideals enough? As a counterpart to the German system of militarism and morals, and as the basis of a system of intellectual culture, they are excellent, but by themselves are they sufficient to satisfy the aspirations of men who seek for higher culture? And who can deny that men, no matter in what station of life they may be placed, have not got innermost thoughts of that kind?

To hold the view that the sole purpose of our Empire in the past has been to give all men within its bounds an English mind is undoubtedly a correct interpretation of our policy of granting that larger freedom which we associate with our race; but what of the future? What have we to offer as a substitute for the ideals of Germany in the intellectual dominion or for the advancement of human welfare? The answer is, of course, nothing.

The shock of the great War must assuredly have awakened us to the responsibility which we, as the rulers of a great Empire, have assumed, and to the realisation of the fact that our shortcomings in the intellectual sphere of activity are many. And to what is it due? To the Party system of government. To the belief that all wisdom was centred in the framers of political constitutions, and in allowing the initiative in all matters pertaining to the development of science, education, and industry to remain with them. Our time has been wasted in waiting for the settlement of political quarrels; have we learnt our lesson? Will the leaders of British industry and science come together and work for the good of the nation and Empire? Will they open up a new outlook and set of ideals of British origin for the Empire so that all who may come within its sway may look at the things of life from the standpoint of a Briton?

It cannot be said that attempts have not been made. Take that remarkable address of Sir Norman Lockyer's to the British Association at Stockport in 1903 on the Influence of Brain Power on History. It is almost prophetic in detail, but yet how many people are there who have absorbed its significance? Very few indeed. Very many may have realised its importance, but have been content to leave its development to the Party system of government. To leave the initiative with the Government in these matters is, we believe, wrong in principle, for the officials cannot be expected by the nature of the work which they follow to have the requisite experience and knowledge to enable them to follow the development of the problems at issue to their logical conclusion. The officials must first of all give consideration to the political views of those who control the Government, and whenever such considerations intervene in questions relating to the development of industry and of science impartial judgment cannot be exercised.

But apart from this it cannot be expected that the members of the Government or their officials can be the best judges of the working conditions which are best suited for the progress of national welfare in industry and science. These questions are not political in character—they are essentially practical; hence they require the practical and scientific mind to evolve them. This brings us to the conclusion, therefore, that the leaders of industry and science must establish their own organisation so as to retain the

initiative in their own hands, and to shape out the working conditions essential for the nation's progress and welfare, and incidentally for the progress and welfare of the Empire, in co-operation with the Government of the day, or without. In this age the greatness of a nation is determined by its intellectual efficiency and by the guidance which it can give to the inhabitants of the weaker States in the progress of human welfare. Shall we again resume that task in this sphere of activity?

"Dream ye of peaceful sway?  
Dream on, who dream it may.  
War still is empire's word!  
Peace? by the Victor's sword!"

As we have already indicated, the working conditions in which we lived prior to the declaration of war have undergone considerable modification and we hope will never return.

We have had a few prophets amongst us who have foreseen the present crisis, and had we followed their advice the present War would not have been possible. In the military sphere of activity we have had Lord Roberts; in the intellectual we have had Sir Norman Lockyer and Professor Cramb; and we have also had the crusade by the Tariff Reformers. The failure of the campaign initiated by the latter group is due entirely to their want of appreciation of the intellectual factors. Several well-known Tariff Reform writers and politicians consider for instance that the great progress made by Germany is entirely due to her fiscal system, and they draw the same analogy with regard to the United States. We have had Tariff Reform excursions to Germany in order to show our workmen the excellent conditions in which German workmen lived, and how prosperous they had become under the system of protection. To attribute the great prosperity of German and American industry primarily to protection is wrong—it is primarily due to the high standard of their intellectual qualities. One is, however, a reflex of the other, and neither can succeed alone. When the War is finished we shall have to consolidate our position, and how is it to be done? There has never been a period in our history, like the present, when it was more essential to have a clear conception of what Empire means. The permanence and prosperity of the Empire can only be made secure by strengthening its basis with brains, science, education, and the organisation of its industrial and national resources. Fiscal measures are secondary considerations, which can be employed as occasion serves to strengthen the props upon which the Empire should in reality be based.

#### NOTE ON A FORMULA FOR THE CALCULATION OF THE ATOMIC WEIGHTS.

By ARTHUR W WARRINGTON,  
Professor of Chemistry at the Kao Teng Hsueh Tang, Chengtu;  
formerly Professor of Natural Philosophy at the Shanxi University;  
and sometime Assistant Lecturer at the University College of  
Wales, Aberystwyth.

LIVING at a distance from centres of scientific investigation and having little leisure for reading, the writer apologises should he unwittingly be retailing stale news.

The approximate atomic weights can be calculated from the following formula:—

$$X = -1 + 2Y + 0.008 Y^2;$$

in which X is the approximate atomic weight, and Y is the number of the element, assuming that there are only eighty-five elements between helium and uranium.

The elements can be arranged in the seven periods shown in the accompanying table.

While the above formula does not give any means of checking the accuracy of the determination of the atomic weights, it does suggest that the number of elements up to and including uranium is limited to eighty-eight.

I.		II.		III.		IV.		V.		VI.		VII.	
2	—	10	Ne	18	—	36	—	54	X	65	—	83	—
2½	He	10½	—	18½	K	36½	Kr	54½	—	65½	—	83½	—
3	—	11	—	19	Ca, A	37	—	55	Cs	66	—	84	—
3½	—	11½	Na	19½	—	37½	Rb	55½	—	66½	—	84½	—
4	Li	12	Mg	20	—	38	—	56	—	67	—	85	Ra
4½	—	12½	—	20½	—	38½	Sr	56½	Ba	67½	—	85½	—
5	Be	13	—	21	Sc	39	Y	57	La	68	Yb	86	—
5½	—	13½	Al	21½	—	39½	Zr	57½	—	68½	—	86½	Th
6	B	14	Si	22	—	40	—	58	—	69	—	87	—
6½	C	14½	—	22½	Ti	40½	Nb	58½	—	69½	—	87½	—
7	—	15	P	23	—	41	—	59	—	70	—	88	—
7½	N	15½	S	23½	—	41½	Mo	59½	—	70½	—	88½	U
8	—	16	—	24	V, Cr	42	—	60	—	71	Ta	—	—
8½	—	16½	—	24½	—	42½	—	60½	—	71½	—	—	—
9	—	17	Cl	25	—	43	—	61	—	72	W	—	—
9½	F	17½	—	25½	Mn	43½	Ru	61½	—	72½	—	—	—
				26	Fe	44	Rh	62	—	73	—	—	—
				26½	—	44½	—	62½	—	73½	—	—	—
				27	Co, Ni	45	—	63	—	74	Os	—	—
				27½	—	45½	Pd	63½	—	74½	—	—	—
				28	—	46	Ag	64	—	75	Ir	—	—
				28½	—	46½	—	—	—	75½	Pt	—	—
				29	Cu	47	—	—	—	76	Au	—	—
				29½	Zn	47½	Cd	—	—	76½	—	—	—
				30	—	48	—	—	—	77	Hg	—	—
				30½	—	48½	In	—	—	77½	—	—	—
				31	—	49	—	—	—	78	Tl	—	—
				31½	Ga	49½	—	—	—	78½	—	—	—
				32	—	50	Sn	—	—	79	Pb	—	—
				32½	Ge	50½	Sb	—	—	79½	Bi	—	—
				33	—	51	—	—	—	80	—	—	—
				33½	As	51½	—	—	—	80½	—	—	—
				34	—	52	—	—	—	81	—	—	—
				34½	—	52½	—	—	—	81½	—	—	—
				35	Se	53	Te, I	—	—	82	—	—	—
				35½	Br	53½	—	—	—	82½	—	—	—

J. J. Thomson's highly suggestive theory of the constitution of the atom leads us to the conclusion that there will be no exact mathematical relation between the atomic weights. From Mayer's arrangements of the magnets (see J. J. Thomson's "Electricity and Matter," p. 116), we are led to believe that two elements having approximately the same atomic weights may have very similar or very dissimilar properties. Groups 3, 8, 13 and 4, 8, 12 contain the same number of magnets, and would thus, according to J. J. Thomson, represent elements having the same atomic weights and belonging to different groups in the Periodic Law.

It is possible that the subject is worthy of the attention of a mathematician.

Chengtu, November 16, 1914.

## EXPANSION OF CHEMICAL AND DYE-STUFF INDUSTRY IN UNITED STATES.\*

(Concluded from p. 107).

**Coal-tar Products.**—Benzol, toluol, and the like are produced in sufficient amount in present installations of by-product coke ovens to provide all of these things that would be needed for a coal-tar chemical industry of a magnitude sufficient to supply the United States market; the separation of these materials from the gas that carries them is dependent upon the market and the demand therefor. There is no inherent defect in our coke industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol, and the like contained in the

gas as a fuel than to separate them from each other for purposes of sale. Ample supply can be provided before any plant that could use benzol and the like for dye-stuff making could be erected in the United States, and thereafter the supply of these materials can readily be kept up to any requirements.

The materials of the preceding paragraph are the ones used in the coal-tar explosives industry, as well as in the coal-tar medicinals and dye-stuffs industries. Each of these three industries co-operates with the others to make full use of those materials, alone none can fully make use thereof nor succeed; the correct and proper utilisation of these materials requires successful co-existence of all three industries in one and the same country.

Naphthalene and anthracene are contained in the tars produced in the United States in an amount sufficient for the needs of a domestic dye-stuff industry, and it is merely a question whether it is more profitable to leave them in the creosote oil, where they now occur, or to separate them out of such oil and refine them for purposes of dye manufacture. Ample supply of either of them could be produced and provided at the same time or shortly after any plant could be erected in the United States for the use of these things in the production of dyes.

What has been said with regard to the supplies of naphthalene is also true of the supplies of cresol.

All the creosote oil contained in the total amount of coke-oven tar now made is separated from it and used. Increased production of creosote oil requires a greater production of tar, and a greater production of tar is dependent upon increased installation of recovery coke ovens.

Phenol or carbolic acid supply is primarily dependent upon our deliberately selected method of coal treatment; to change that treatment so as to get more phenol would entail abandonment of other advantages which would not be compensated for by the increased amount

\* From the *Chemical Engineer*, xx., No. 6.



of phenol so produced. Under present circumstances freights and haulages play an important part. At isolated plants, separated by considerable distances from each other, small amounts of phenol are produced, and the separation of the phenol at such individual places would be economically unprofitable, and in order to concentrate this amount of phenol to or at a point where separation could be conducted profitably would entail freight haulages much in excess of the value of the phenol that would thus be transported.

The only source of phenol in sight is that produced synthetically from benzol by means of sulphonation and subsequent melting with caustic soda; this depends in turn upon our benzol supply, and would be profitable only so long as the United States market is not killed by the dumping of foreign phenol thereon, whether such phenol be synthetic or distilled.

Salicylic production depends upon availability of phenol, and the production of benzoic acid depends upon the availability of toluol, which has heretofore been discussed.

Phthalic acid made from naphthalene by means of bichromate cannot successfully compete with the mercury and sulphuric acid process, which is protected by patents having about three years more to run.

#### *Miscellaneous Chemicals and Raw Materials.*

*Acetic anhydride* can be made without trouble in this country, and will be made in this country so soon as the domestic demand is large enough and steady enough to warrant the installation of a suitable plant,

*Nitric Acid.*—All countries with the exception of possibly Norway and the countries importing from Norway are dependent upon Chile for the raw material for making nitric acid. It will not be profitable to make nitric acid from air in the United States until the value of the electric horse-power reaches a level of 3 or 4 dols. a year, as it is in Norway.

*Ammonia* and its salts all depend upon recovery coke-ovens, and such recovery plants are increasing as fast as circumstances will permit.

*Barium chloride* and other compounds of barium may be made from domestic barytes. A number of attempts have hitherto been made, but with indifferent success. Factories established within the last year promise to be successful.

*Magnesium chloride* of a sufficient purity to be used in the production of flooring is almost generally made from magnesite found in Greece, which is the only deposit known having sufficiently high purity; there are reports of suitable deposits in California and in Lower California, and with the completion of the Panama Canal the question of freights, which seems hitherto to have stood in the way of developing these deposits, may be eliminated. Other sources, less remote from centres of consumption, and using other materials, e.g., brine waste, are about to be successfully operated.

*Manganese* in the form of pyrolusite is not known to occur in paying deposits in the United States; these are practically all in the Caucasus.

*Potash.*—In view of the great exertions that have been made for a number of years, both on the part of the Federal Government through a number of its departments and a great many different groups of capitalists, there is nothing to be said in this report that would be of any value with regard to increased production of potash either as fertiliser or as a chemical.

*Yellow prussiate* and sodium cyanide can be and have been made from domestic materials in such an amount as to provide practically the entire consumption or a great portion thereof in this country so long as there was a sufficient duty on them; the present duty is not enough to protect the American manufacturer, and those who were engaged therein have in large measure withdrawn from the business, but some are reported to be taking up manufacture cautiously and in limited amount.

*Hydrosulphites* in solution can be made from domestic materials without interference with any patent rights; the production of solid salts and derivatives are, however, still protected by patents that have a few years more to run.

*Sodium nitrate* is produced more cheaply as a by-product in Norway than it can be produced anywhere in the world; unless the price of the electric horse-power in this country sinks to 3 or 4 dols. level per year, as in Norway, this product cannot be manufactured in the United States.

*Oxalic acid* is and has been made to some extent in this country, and the information coming to your Committee is that suitable efforts are being made to expand the capacity of existing plants.

*Tartaric Acid and Citric Acid.*—To make this country independent of others with respect to tartaric acid and citric acid would call for radical changes on the part of our grape growers and our lemon growers as to the policy of their business.

It is probably true that edible grapes do not produce argols (the crude material for tartaric acid) very largely, and that our domestic lemons do not produce as large yields of juice (the crude material for citric acid), nor as high an acidity as do the Italian lemons; therefore an independent supply of the raw materials produced in the United States for tartaric and citric acids is, in the first instance, an agricultural problem, and in the second instance a market problem.

#### *General Remarks.*

Finally, it should be pointed out that the United States is by no means the only country whose chemical and allied business has been strained or upset by the European war. Each and every other country has felt the strain. British committees have gone into this same subject of expanding British chemical industries, and not only that, but also into the question of making their very basic necessities, and the reports have so far been adverse to any immediate relief by domestic manufacture. The Boston Chamber of Commerce, through its Committees, has arrived at the same conclusion for this country.

It is further clear that the stability of a complete domestic chemical industry, in so far as it depends upon foreign supplies, is bound up to a successful merchant marine and to an efficient foreign banking condition, just as is all our foreign business.

#### *Findings.*

Your Committee finds as follows, as to the facts:—

1. Prior to the hostilities domestic chemical industry was utilising and exploiting every reasonable opportunity to its full extent.
2. Since the outbreak of hostilities domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome.
3. Since the outbreak of hostilities domestic plants that had heretofore been shut down or partly dismantled because of disastrous foreign competition are said to have resumed operation with caution.
4. That a 30 per cent duty on some coal-tar dyes for over thirty years has not produced a real coal-tar dye industry in this country.

#### *Conclusions.*

Your Committee submits its conclusions as follows:—

A. To prevent the unfair underselling alleged to be practised by foreigners in this country, the adoption of an effective anti-dumping clause.

B. The so-called coal-tar "intermediates" which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinals, and dye-stuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes; all coal-tar dyes without exception to be taxed alike, namely, 30 per cent *ad valorem* and 7½ cents per pound specific.

C. Changes in the patent laws, such as by compulsory licensing or compulsory working clauses, are wholly ineffective, do more harm than good, and should not be attempted.

Your Committee recommends that this report be submitted to the appropriate committees of Congress. Further, that this report be forwarded to interested parties.

# THE CONSTITUTION OF SOME NITROGEN AND PHOSPHORUS COMPOUNDS, AND THE CONSTITUTION OF ELEMENTARY PHOSPHORUS.

By GERVAISE LE BAS, B.Sc. (Lond.).

## Hyponitrous Oxide, N<sub>2</sub>O.

The formula for hyponitrous oxide cannot be any other than—



So far as we know, this has never been verified. The theory of molecular volumes enables us to do so.

We may obtain an approximate value for N<sub>2</sub>O at the boiling-point by means of D. Berthelot's formula from the critical data—

$$V = \frac{11.1 T_c^2}{P_c(2T_c - T)} = \frac{11.1 \times 309 \times 30.9}{73.6(618 - 183)} = 33.1.$$

Since N = 15.6, O = 8.3 (*Phil. Mag.*, Feb., 1914, p. 346).

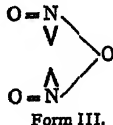
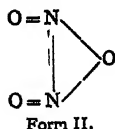
2 N	..	..	..	..	31.6
O	..	..	..	..	8.3
					—
Σ <sub>n</sub> V <sub>a</sub>	..	..	..	..	39.9
V <sub>m</sub>	..	..	..	..	33.1

Contraction for □<sub>3</sub> .. .. -6.8

The molecule of hyponitrous oxide thus contains a three membered ring (*Phil. Mag.*, xxvii., 453, October, 1914).

## Nitrous Anhydride.

N<sub>2</sub>O<sub>3</sub> .. .. B.p. 3.5 d<sub>0</sub> 1.45 (*Chem. Kal.*)  
V<sub>m</sub> 52.4

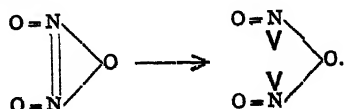


2N	..	..	31.6
3O	..	..	24.9
			—
			56.5
Less for ring			-6.5
Σ <sub>n</sub> V <sub>a</sub>	..	..	50.0
			—
			-2.4

V<sub>m</sub> 52.4

2N	..	..	31.6
2O"	..	..	16.6
>O	..	..	5.0
			—
Σ <sub>n</sub> V <sub>a</sub>	..	..	53.2
			+0.8

The observed volume is slightly below the value for compound constituted as in Form II. From this it is concluded that Form II. is true and that the following change takes place:—



## Elementary Phosphorus, P<sub>4</sub>.

The volume of phosphorus, on the supposition that its atomic value is 27.0, would be—

$$P_4 = 108.0.$$

We thus find—

P <sub>4</sub> (elem.)	..	..	83.6
P <sub>4</sub> (combined)	..	..	108.0
			—
			-24.4

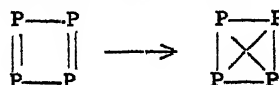
That is, there is a large contraction of -24.4. This cannot be explained by means of the formula—



for its molecular volume would, on this assumption, be—

4P	..	..	..	108.0
Less for □ <sub>4</sub>	..	..	..	8.5
				—
Σ <sub>n</sub> V <sub>a</sub>	..	..	..	99.5
V <sub>m</sub>	..	..	..	83.6

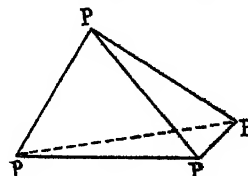
This formula, however, may be changed thus—



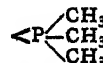
The latter formula possesses three three-membered rings. The molecular volume would be—

4P	..	..	..	108.0
Four □ <sub>3</sub> rings	..	..	..	-26.0 (4 × 6.5)
				—
Σ <sub>n</sub> V <sub>a</sub>	..	..	..	82.0
V <sub>m</sub>	..	..	..	83.6

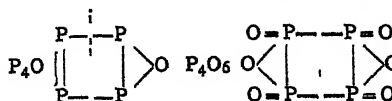
An interesting explanation can be given to the cross-linked formula. It is really equivalent to a tetrahedron with a phosphorus atom at each corner.



It follows that the directions of the valency links are along the edges of this tetrahedron. This applies to all trivalent atoms, and enables us to obtain a configuration of the molecules of their compounds.



Starting from hyponitrous oxide and the corresponding hypophosphorus oxide, we can explain the formulae of those phosphorus oxides which possess ring structure.



d<sub>25</sub> 1.936 b.p. 173 C=45 V<sub>m</sub> 130.6 by form.

4P .. .. .	108.0
4O .. .. .	33.2
2>O .. .. .	10.0

Less for □<sub>4</sub> .. .. . 151.2  
-8.5

Less for 2 □<sub>3</sub> .. .. . 142.7  
-13.0

Σ<sub>n</sub> V<sub>a</sub> .. .. . 129.7  
V<sub>m</sub> .. .. . 130.6

Both of these compounds indicate that, at least in the nascent state, the simpler compound exists:—



## THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.\*

By O. L. BARNEBEY.

SINCE the original proposal of the permanganate titration of iron by Marguerite (Ref. 1),† the method has undergone various modifications. The majority of these changes were made to obviate the high results obtained by titrating in the presence of hydrochloric acid. This error was first pointed out by Löwenthal and Lenssen (2), and later by a number of authors (3, 26). Kessler (4) first called attention to the fact that considerable sulphuric acid, and still better manganese salts, greatly reduced the influence of the hydrochloric acid. Zimmerman (5) then proposed the use of manganese salts for this purpose, claiming as great an accuracy in hydrochloric as in sulphuric acid solutions. Reinhardt (7) next suggested the use of phosphoric acid also, for the removal of the colour of ferric chloride to ensure a better end-point.

The permanganate method, used very largely to-day for the determination of iron in ores, in brief is as follows:—Solution of the ore by heating with stannous chloride and hydrochloric acid, completion of the reduction by adding stannous chloride to the hot solution until colourless, dilution, addition of mercuric chloride to remove the excess of stannous salt, addition of the Zimmerman-Reinhardt solution (sometimes known as "preventive solution") containing sulphuric acid, manganese sulphate, and phosphoric acid, and titration with permanganate, taking the first recognisable tint of colour, permeating the entire solution for a short time, as the end-point (inasmuch as the end-point is somewhat unstable in the presence of chlorides),

The question which has concerned most of the authors quoted is:—Does the Zimmerman-Reinhardt or similar solution really prevent the action of hydrochloric acid? Birch (23) maintains that the method is only an approximate one. However, the consensus of opinion of the various workers is that, if used in sufficient quantity, it stops practically all, if not all, of the influence of small amounts of hydrochloric acid. Friend (24) says the concentration of hydrochloric acid should not be greater than 0.25 M. Jones and Jeffreys (22) find a constant error, which is not obviated by any concentration of hydrochloric acid or manganese sulphate mixture. They recommend a subtraction of this error in each determination. To test this point, a standard solution of ferrous sulphate, containing sulphuric acid, was prepared, and its strength determined by permanganate titration in sulphuric acid solution. Equal volumes of this solution were then

employed for titration with varied quantities of hydrochloric acid and preventive solution.

### General Reagents.

The Reinhardt-Zimmerman solution was made as follows:—160 grms. of crystallised manganese sulphate, 330 cc. phosphoric acid (sp. gr. 1.17), and 320 cc. of sulphuric acid (sp. gr. 1.84) diluted to 2400 cc. It is also designated manganese solution No. 1, to distinguish it clearly from other preventives employed. This solution is in general use for the titration of iron.

Other reagents used in this and other series are as follows:—Hydrochloric acid, sp. gr. 1.10; sulphuric acid, sp. gr. 1.40; phosphoric acid, sp. gr. 1.35; mercuric chloride, a saturated solution; stannous chloride, 200 grms. SnCl<sub>2</sub>.2H<sub>2</sub>O, and 70 cc. HCl (sp. gr. 1.20) per litre.

The ferric chloride solutions used in each series following series six were analysed by the use of the Zimmerman-Reinhardt solution called in this paper "manganese solution No. 1." At least one result is given in each series. Where only one result is given it is an average of two or more analyses.

Special reagents for individual series will be described in connection with the series in which they are used.

### Volume of Solutions Titrated.

Unless otherwise stated, the volume of the solution after dilution just preceding titration was about 500 cc. In most cases a considerable deviation from this volume is of very little consequence, but for the general purposes of this paper it is important.

### Use of Preventives containing Manganese.

Table I. shows very concretely that no correction for an inherent error of the Zimmerman-Reinhardt method is necessary. However, it is easy to conceive a trace of iron in a reagent such as the stannous chloride, which, if used for the reduction of all the iron present, would introduce a fairly uniform error of the nature described by Jones and Jeffreys (22).

A number of authors recommend a time interval between the addition of the mercuric chloride and manganese sulphate solution. In some cases even ten minutes (26) is designated. This was investigated by titrating:—(a) with a time interval of twenty seconds, (b) of thirty seconds, (c) of ten minutes, using the solutions employed in Table I. In (a) and (b) vigorous stirring with a rather heavy glass rod accompanied the addition of the tin salt, and continued until the end of the titration.

These results show that only a short interval of time is necessary between the addition of stannous chloride and mercuric chloride, if the solution is thoroughly agitated.

### Speed of Titration.

Many series of analyses have been made in which the influence of the speed of titration was closely watched. In this study the permanganate was added at as nearly a uniform rate as possible until the end-point was closely approached, and then the titration was finished more slowly. The solutions were stirred vigorously during the entire titration to give uniformity of mixing. Series III. is typical of the results obtained.

Another of the several series of analyses was performed using ferrous sulphate as the standard iron solution with analogous results.

The results of Series III. seem to justify the conclusion that, if the action of the hydrochloric acid has been offset by a sufficient excess of the preventive, no difference enters except the difference in burette drainage. (See also Series I.). However, if the amount of preventive just sufficient for a good result with considerable hydrochloric acid present in a slow titration be used under the same conditions, except in a faster titration, then more permanganate is required. This confirms the work of Friend (24).

\* From the *Journal of the American Chemical Society*, xxxvi., No. 7.

† The References will be given at the end of the article.

TABLE I.

Series I.—Accuracy of the Zimmerman-Reinhardt Method.

20 cc.  $\text{FeSO}_4$  solution = 0.1338 gm. Fe. 1 cc. of  $\text{KMnO}_4$  solution = 0.004386 gm. Fe. (a)

Expt. No.	Weight Fe taken.	HCl. Cc.	$\text{H}_2\text{SO}_4$ . Cc.	Manganese solution No. 1. Cc.	$\text{SnCl}_2$ . Cc.	$\text{HgCl}_2$ . Cc.	Weight Fe found.	Deviation from $\text{H}_2\text{SO}_4$ result.
1.	0.1338	—	20	—	—	—	0.1338	—
2.	0.1338	—	20	—	—	—	0.1338	—
3.	0.1338	—	20	20	—	—	0.1337	-0.0001
4.	0.1338	5	—	20	—	—	0.1338	—
5.	0.1338	10	—	20	—	—	0.1337	-0.0001
6.	0.1338	10	—	20	—	—	0.1337	-0.0001
7.	0.1338	25	—	20	—	—	0.1339	+0.0001
8.	0.1338	40	—	20	—	—	0.1351	+0.0013
9.	0.1338	5	—	—	—	—	0.1368	+0.0030
10.	0.1338	10	—	20	0.06	10	0.1338	—
11.	0.1338	10	—	20	0.10	10	0.1337	-0.0001
12.	0.1338	10	—	20	0.20	10	0.1338	—

(a) This is the average value obtained by checking the solution against electrolytic iron, sodium oxalate, and ferrous ammonium sulphate. All the permanganate solutions used in this investigation were standardised in a similar manner.

TABLE II.

Series II.—Interval of time necessary just before titration. 1 cc.  $\text{KMnO}_4$  = 0.004386 gm. Fe. 20 cc.  $\text{FeSO}_4$  (=0.13 gm. Fe) + 10 cc.  $\text{HCl}$  + 10 cc.  $\text{HgCl}_2$  + 20 cc. Mn solution No. 1 taken.

No.	$\text{SnCl}_2$ . Cc.	Time interval.	Weight of Fe found.
1.	0.06	20 sec.	0.1338
2.	0.10	20 sec.	0.1340
3.	0.10	30 sec.	0.1338
4.	0.10	30 sec.	0.1338
5.	0.10	10 min.	0.1338
6.	0.10	10 min.	0.1340

Series III.—Effect of speed of titration. 1 cc.  $\text{KMnO}_4$  = 0.004836 gm. Fe. 20 cc.  $\text{FeCl}_2$  (=0.1717 gm. Fe). 10 cc.  $\text{HCl}$  taken.

Mn solution No. 1.		Time.		Weight Fe found.
Cc.		Min.	Sec.	Gm.
20		2	30	0.1717
20			45	0.1718
		2	30	0.1717
5			45	0.1732
3		2	0	0.1719
3			45	0.1739
2		2	30	0.1729
2		1	45	0.1727
2		1	10	0.1732
2			45	0.1739
2			10	0.1755

This solution contained 10 cc.  $\text{HCl}$  (1.2) per litre.

In the work outlined in the following the solutions were stirred thoroughly, and the burette allowed to give a uniform flow of permanganate until the end-point was nearly approached, then the titration was finished more slowly, as indicated above. About 1 cc. for each 2 seconds was the rate adopted as a convenient basis for comparison of results.

#### Effect of $\text{HgCl}$ in Suspension.

In a large number of titrations, in which an amount of preventive insufficient to stop the action of hydrochloric acid on the permanganate was used, a partial or complete disappearance of the calomel was noticed. This suggested the action of chlorine or hypochlorous acid on the mercurous chloride, thus reducing the concentration of active oxidising agent in solution, and correspondingly lowering the speed of oxidation of ferrous iron, hence requiring more permanganate to complete the reaction. To test this, measured portions of standard ferric chloride

solution were acidified with 10 cc. of hydrochloric acid (sp. gr. 1.10), heated, reduced with stannous chloride as usual, and diluted; mercuric chloride was added, and the calomel filtered out. To the filtrates were added varying amounts of stannous chloride (40 grms. per litre), and the titration was finished as before indicated. No preventive was used in this series. Meineke (11) likewise calls attention to the influence of calomel on the titration.

All the end-points were indefinite, becoming more so as the quantity of calomel increased. The first semi-permanent tinge throughout the solution was taken as the end-point. These results show that when the hydrochloric acid is allowed to interfere in titration the amount of interference is somewhat proportional to the concentration of calomel in suspension.

TABLE III.

Series IV.—Effect of suspended calomel.

Expt. No.	Weight of Fe taken.	$\text{HCl}$ . Cc.	$\text{HgCl}$ . Cc.	Excess of $\text{SnCl}_2$ . Cc.	Weight of Fe found.
1.	0.1930	10	20	1	0.2039
2.	0.1930	10	20	1	0.2035
3.	0.1930	10	20	2	0.2075
4.	0.1930	10	20	3	0.2101
5.	0.1930	10	20	3	0.2105
6.	0.1930	10	20	5	0.2149

#### Quantity of Manganese Solution required.

A series of analyses was made by reducing measured portions of a ferric chloride solution, adding the other reagents as in Series III., but using varying quantities of the manganous sulphate solution mixture. Another series was made keeping the manganous sulphate solution constant. In each determination one drop of stannous chloride was added in excess, and the resulting calomel left in suspension.

The lower limit of accuracy under the conditions obtaining is seen to be 6 cc. of manganese solution mixture for 5 cc. of hydrochloric acid added to the other chlorides present. This amount would probably be somewhat different for varying quantities of ferric chloride, and slightly varying with different individuals because of differences in manipulation.

#### Manganese Solutions with and without Phosphoric Acid.

A manganese sulphate solution containing 160 grms of crystallised salt in 2400 cc. was prepared and used in the following series. (This solution is designated "manganese solution No. 2").

TABLE IV.

Series V.—Quantity of manganese sulphate solution required. 1 cc. of  $\text{KMnO}_4 = 0.004887$  grm. Fe. 20 cc. of  $\text{FeCl}_3 (= 0.2290$  grm. Fe) + 10 cc.  $\text{HgCl}_2$  taken.

HCl. Cc.	Manganese solu- tion No. 1. Cc.	Weight of Fe found.	Comments.
5	—	0.2346	End-point unstable.
5	1	0.2331	
5	2	0.2314	
5	3	0.2302	End-point more stable.
5	4	0.2299	
5	5	0.2299	
5	6	0.2290	End-point good.
	6	0.2287	
	10	0.2287	
5	20	0.2290	Part of $\text{HgCl}$ dissolved.
5	20	0.2290	
5	20	0.2290	
10	20	0.2292	
15	20	0.2290	
20	20	0.2292	
25	20	0.2290	
30	20	0.2292	
35	20	0.2292	
40	20	0.2299	
50	20	0.2316	
55	20	0.2316	
60	40	0.2297	All of $\text{HgCl}$ dissolved.
75	40	0.2302	
75	40	0.2302	
120	80	0.2321	

TABLE V.

Series VI.—Use of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  with  $\text{MnSO}_4$ . 1 cc.  $\text{KMnO}_4 = 0.004847$  grm. Fe. 20 cc.  $\text{FeCl}_3 (= 0.2101$  grm. Fe, Experiments 1—15 inclusive) and 20 cc.  $\text{FeCl}_3 (= 0.2310$  grm. Fe, Experiments 16—28 inclusive) + 10 cc.  $\text{HCl}$  + 10 cc.  $\text{HgCl}_2$  taken.

Expt. No.	Manganese solu- tion No. 2. Cc.	$\text{H}_2\text{SO}_4$ . Cc.	$\text{H}_3\text{PO}_4$ . Cc.	Weight of Fe found.	Deviation
1.	1	—	—	0.2201	+0.0100
2.	2	—	—	0.2205	+0.0104
3.	3	—	—	0.2167	+0.0066
4.	6	—	—	0.2133	+0.0032
5.	10	—	—	0.2133	+0.0032
6.	15	—	—	0.2128	+0.0027
7.	25	—	—	0.2118	+0.0017
8.	50	—	—	0.2101	—
9.	50	—	—	0.2194	+0.0003
10.	25	12	—	0.2101	—
11.	15	8	—	0.2104	+0.0003
12.	10	5	—	0.2133	+0.0032
13.	10	15	—	0.2121	+0.0020
14.	10	30	—	0.2106	+0.0005
15.	10	50	—	0.2123	+0.0022
16.	—	12	—	0.2375	+0.0065
17.	—	12	—	0.2382	+0.0072
18.	—	—	12	0.2363	+0.0053
19.	—	—	12	0.2375	+0.0074
20.	25	—	—	0.2322	+0.0012
21.	25	—	10	0.2307	-0.0003
22.	25	—	10	0.2307	-0.0003
23.	25	—	—	0.2322	+0.0012
24.	25	—	5	0.2310	—
25.	25	5	—	0.2312	+0.0002
26.	25	5	—	0.2312	+0.0002
27.	25	5	—	0.2310	—
28.	25	—	5	0.2310	—

This series shows (a) that manganese sulphate without sulphuric or phosphoric acid will prevent the effect of hydrochloric acid on the permanganate, (b) that a less amount of manganese sulphate is required when it is

accompanied by sulphuric or phosphoric acids, and (c) that sulphuric and phosphoric acids can be used interchangeably.

On account of the fact shown in Series V., that the phosphoric and sulphuric acids could be used interchangeably, it seemed worth while to make a solution of manganese sulphate in sulphuric acid, and test its prevention. Consequently, a solution was prepared containing 70 grms. of crystallised salt and 300 cc. sulphuric acid (sp. gr. 1.84) per litre). (This solution is designated "manganese solution No. 3").

These results show that the use of phosphoric acid is merely a matter of preference. Except in the cases where 40 cc. of hydrochloric acid was present, one solution seemed to be as good as another: however, in the latter case, what difference does exist is in favour of the phosphoric acid. Of course, no such volumes of hydrochloric acid are used in the analysis of iron ores, making this point of less consequence.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 18, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Gaseous Combustion at High Pressures." By Prof. W. A. BONE, F.R.S., and others.

The paper gives an account of investigations carried out with an installation of apparatus specially designed for the purpose.

Mixtures of methane with less than its own volume of oxygen were exploded in steel bombs at initial pressures of between 8 and 32 atmospheres. The results were in harmony with the "hydroxylation" theory of hydrocarbon combustion put forward some years ago by Prof. Bone. The influence of various secondary reactions upon the products of primary oxidation whilst the gases are cooling down after attainment of maximum pressure is discussed in the light of the experimental results.

Results of experiments upon an equimolecular mixture of ethane and oxygen, whose behaviour is crucial in respect of the different views of hydrocarbon combustion advanced in recent years, have again confirmed the hydroxylation theory.

Another section of the paper deals with an experimental determination of the relative affinities of methane, hydrogen, and carbon monoxide for oxygen in flames. It is shown (1) that the affinity of methane is at least twenty times as great as that of hydrogen; (2) that when mixtures corresponding to  $\text{CH}_4 + \text{O}_2 + x\text{H}_2$  are fired under high initial pressures, in which the partial pressures of methane and oxygen are kept constant and  $x$  only varied, the distribution of oxygen between the methane and hydrogen varies with  $x^2$ —which means that hydrogen is burnt *directly* to steam in flames as the result of the tri-molecular change  $2\text{H}_2 + \text{O} = 2\text{H}_2\text{O}$ , and not (as some have supposed) *indirectly* through hydrogen peroxide.

The affinity of carbon monoxide is shown to be comparable with that of hydrogen for oxygen in flames.

Experiments are described in which mixtures of ethylene, oxygen, and hydrogen, corresponding to  $\text{C}_2\text{H}_4 + \text{O}_2 + x\text{H}_2$ , were exploded at high initial pressures; *inter alia* it was found possible to increase  $x$  up to 8 without causing deposition of carbon on explosion. The theoretical bearing of the results is discussed.

The final section describes experiments in which the whole pressure curves, up to and far beyond the attainment of maximum pressure, were recorded when mixtures



corresponding to (1)  $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ , (2)  $2\text{CO} + \text{O}_2 + 4\text{N}_2$ , and (3)  $\text{CH}_4 + \text{O}_2 + 4\text{N}_2$  are exploded under initial pressure of about 50 atmospheres. The rates of attainment of maximum pressure in each case have no direct relation to the order of affinities of the various gases for oxygen.

*"The Orbits of a Charged Particle round an Electric and Magnetic Nucleus."* By Prof. W. M. HICKS, F.R.S.

Two problems are discussed—the orbits of  $\alpha$ -particles and the orbits of electrons round nuclei containing mass, a definite number,  $n$ , of positive electronic charges, and a definite number,  $N$ , of co-axial magnetons—the motion being in their equatorial planes.

It is found that combined systems (atoms) with  $\alpha$ -particles may exist in which the  $\alpha$ -particle revolves in permanent connection with the nucleus, provided the internal energy of the atom is greater than a certain critical value, and that states of "radio-active" instability occur in which, after a combination of long duration, the  $\alpha$ -particle is shot off to infinity. The exact velocity of emission in any case depends on the values of the  $n$ ,  $N$ , but it is of the order of magnitude of the velocity of emission of  $\alpha$ -rays from radium.

In the case of electronic orbits, in addition to the combined systems with internal energy less than from infinity, there can exist also permanent systems in which the internal energy is greater than that from infinity, although less than a certain critical amount, and in which again states of "radio-active" instability occur of the proper order of magnitude.

We are scarcely yet in a position profitably to attempt to formulate a definite theory of the nuclear structure of the atom. Before this is possible, scientific imagination has to be guided by definite knowledge as to the properties of a number of special cases susceptible of accurate mathematical analysis. It is merely as a contribution to such a pioneer survey that the present communication is offered.

*"The Lunar Diurnal Magnetic Variation and its Change with Lunar Distance."* By S. OHAPMAN.

Balfour, Stewart, and Schuster have developed a theory of the solar diurnal magnetic variations which attributes them to electric currents in the upper atmosphere, impelled by electromotive forces produced by the motion of the air across the earth's permanent magnetic field. The atmospheric conductivity is supposed to be wholly or partly due to solar influence and varies with the sun's hour angle.

This theory apparently applies also to the lunar diurnal magnetic variations which possess a semi-diurnal component of constant phase, together with other components whose epochs depend on the angular distance between the moon and sun; hence, when averaged over a lunation, all components save the former disappear. The suggested solar influence on the atmospheric conductivity is thus supported, and a semi-diurnal atmospheric oscillation—such as a lunar atmospheric tide—is suggested as the source of the magnetic variations.

Before this theory was developed, Brown ("Trevandrum Observations, 1863") had found that the amplitude of the 12-hour magnetic component at perigee was to that at apogee in the ratio of (lunar distance)—3 at the two epochs—"as in the tidal theory," he briefly remarked; but Figue ("Batavian Observations, 1903") disputed this conclusion. The present paper discusses the evidence, of this direct kind, for or against a tidal origin of these magnetic variations. Brown's and Figue's data are used, together with much newly computed material from other observatories. The total hypothesis is confirmed, although on account of the accidental errors affecting the minute quantities under discussion, the exact law of (distance) $^{-n}$ , with  $n=3$ , is not beyond question, but if  $n$  is assumed necessarily integral, its value is certainly 3 and not 2 or 4.

The investigation also revealed an unexpected phase change of the 12-hour term, the phase at perigee being about  $30^\circ$  ahead of that at apogee. A discussion of the

known facts connected with the lunar magnetic variation fails to afford any explanation, and it is possible that the phenomenon will prove a clue to some important but hitherto unrecognised factors in these magnetic or tidal phenomena.

*"Some Temperature Refraction Coefficients of Optical Glass."* By Lieut.-Col. J. W. GIFFORD.

This is a supplement to a paper read in 1912 in which the refractive indices for 13 wave-lengths of 27 different glass meltings were given by the author. To this table are now added similar indices for six more Jena glass meltings, including those for the recent fluor crown.

This is followed by a table of the temperature refraction coefficients for all the glass meltings dealt with, and attention is drawn to the abnormal coefficient for fluor crown which is a minus quantity.

An attempt is then made to determine, if only approximately, the influence of barometric changes on the refractive powers of optical glass which would seem to be, similarly, a minus quantity, amounting to something like six units in the sixth decimal place only.

## CHEMICAL SOCIETY.

Ordinary Meeting, January 21, 1915.

Prof. W. H. PERKIN, LL.D., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the following losses by death sustained by the Society since the last Ordinary Scientific Meeting: Carl Liebermann (Honorary and Foreign Member), John Henry Baldock, Charles Cochrane Iles (killed in action), John Esson McGillivray, Theodore Maxwell.

Messrs. T. S. Moore, H. Atlas, and H. Ratcliffe were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Walter Thomas Davies, B.A., B.Sc., 115, Station Road, Old Hill, Staffordshire; Robert George Fargher, M.Sc., 34, Myddelton Square, E.C.; Nagardas Purushottam Gandhi, M.A., B.Sc., care of Messrs. Jamal Bros. and Co., Ltd., Rangoon, Burma; Lemuel Lucas Joshi, M.D., B.Sc., Girgaon, Bombay, India; Thomas Morison Maben, 16, Battery Road, Singapore, S.S.; Kenneth George Marsden, B.A., Culloden, Neboda, Ceylon; John William Mitchley, North View, King's Lynn; Charles Smart Roy, Ph.D., 6, Broomhill Road, Goodmayes, Ilford; Sydney Smith, Ph.D., B.Sc., 2, Sunbeam Cottages, Dartford Heath, Dartford; Maurice White, 53, Eastern Road, Romford.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Mammatha Nath Chatterji, Department of Agriculture, Patkapur, Cawnpore, India; Sreenagula Mallannah, H.H. the Nizam's Government, Hyderabad, India.

The following papers were read:—

*"isoQuinoline Derivatives."* Part VIII. *The Constitution of the Reduction Products of Papaverine* (continued). *The Constitution of Pavine.* By FRANK LEE PYMAN.

*"Syntheses of 3-Oxy(1)thionaphthen."* By BROJEN-DHANATH GHOSH and SAMUEL SMILES.

*"The Behaviour of Colloids towards Mixed Liquids."* Part I. *The Systems: Caoutchouc-benzene-alcohol and Caoutchouc-benzene-acetone.* By WILLIAM AUGUSTUS CASPARI.

Ordinary Meeting, February 4, 1915.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Nathaniel Bradley and John Smyth.

Messrs. G. W. Grinling and A. W. Stewart were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Alfred Louis Bacharach, B.A., 7, Strathray Gardens, Eton Avenue, N.W.; Reginald Ernest Essery, B.Sc., 24, Osterley Park Road, Southall; John Ernest Mason, B.Sc., The Old Vicarage, Barlby, Selby; Henry Taylor Fowkes Rhodes, 50, Sydenham Park, Sydenham, S.E.

The following papers were read—

"The Oxidation by Aconitine." By GEORGE BARGER and ELLEN FIELD.

"Azotisation of Chloroamines." By MARTIN ONSLOW FORSTER.

"The Influence of Sucrose and Alkali Chlorides on the Solvent Power of Water." By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

#### Ordinary Meeting, February 18, 1915.

CERTIFICATES were read for the first time in favour of Messrs. Frank Theodore Alpe, Bracondale, Wymondham, Norfolk; Frederick Charles Ball, B.Sc., 50, Hindley Road, Dudley; Harri Heap, M.Sc., Brunside, Lyndhurst Road, Withington, Manchester; Colin Henry Lumsden, B.Sc., Homelea, Sandcliffe Road, Erith, Kent.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Leonard Richmond Wheeler, B.Sc., Queen's Royal College Port of Spain, Trinidad, B.W.I.

The PRESIDENT announced that the following changes in the officers and Council were proposed by the Council:—  
*President to retire*—Prof. W. H. Perkin.

*Vice-Presidents to retire*—Prof. E. J. Mills and Prof. G. T. Morgan.

*Treasurer to retire*—Dr. Alexander Scott.

*Ordinary Members of Council to retire*—Mr. E. J. Bevan, Prof. A. J. Brown, Dr. H. G. Colman, Prof. A. Harden.

*As President*—Dr. Alexander Scott.

*As Vice Presidents who have filled the office of President*—Prof. H. E. Armstrong, Prof. A. Crum-Brown, Sir William Crookes, Sir James Dewar, Prof. Harold B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. Hugo Muller, Prof. W. Odling, Prof. W. H. Perkin, Sir William Ramsay, Prof. J. Emerson Reynolds, the Right Hon. Sir Henry Roscoe, Sir Edward Thorpe, Sir William A. Tilden,

*As Treasurer*—Dr. M. O. Forster.

*As Honorary Secretaries*—Dr. Samuel Smiles and Prof. J. C. Philip.

*As Foreign Secretary*—Prof. Arthur W. Crossley.

*As Vice-Presidents*—Prof. H. Brereton Baker, Dr. Horace T. Brown, Prof. P. P. Bedson, Mr. C. T. Heycock, Prof. F. R. Japp, and Prof. R. Threlfall.

*As New Ordinary Members of Council*—Mr. D. L. Chapman, Prof. F. G. Donnan, Mr. W. Macnab, and Prof. J. F. Thorpe.

Sir James J. Dobbie, Sir Alexander Pedler, and Prof. A. Liversidge were elected Auditors to audit the Society's Accounts.

Prof. T. S. Moore and Mr. R. E. Jackson were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected:—Samuel Culloch Bone; Sidney Albert Brazier, M.Sc.; Neal Brodie, B.Sc.; Frank Buckley; Manmatha Nath Chatterji; Walter Thomas Davies, B.A., B.Sc.; John Gerald Frederick Druce; Robert George Fargher, M.Sc.; James Fraser; Negardas Purushottam Gandhi M.A., B.Sc.; Lemuel Lucas Joshi, M.D., B.Sc.; Reginald Robert Kuntzen; Thomas Morison Maben; Ronald MacInnes; Sreenagula Mallanah, M.D., C.M.; Kenneth George Marsden, B.A.; Frederick Alfred Mason, B.A., Ph.D.; John William Mitchley; Albert Parker, M.Sc.;

Arthur Dawes Robinson, B.A.; Charles Smart Roy, Ph.D.; Harold Gordon Rule, B.Sc., Ph.D.; Ramtaran Sen; Harry Shulman, B.Sc.; Sydney Smith, B.Sc., Ph.D.; John Taylor, M.Sc.; Henry Terrey, B.Sc.; Su-hian Ting; Maurice White.

The following papers were read:—

"Researches on Silicon Compounds. Part IX. Constitution of Silica, Silico-oxalic Acid, and Mesosilico oxalic Acid." By GEOFFREY MARTIN.

"New Halogen Derivatives of Camphor. Part I.  $\alpha$ -Chlorocamphor." By T. M. LOWRY and V. STEELE.

#### PHYSICAL SOCIETY.

Annual General Meeting, February 12, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

The Report of the Council was taken as read.

The Report of the Treasurer was read by Mr. Duddell.

Both reports were put to the meeting and unanimously adopted.

Votes of thanks to the Auditors, the Officers and Council, and the Governing Body of the Imperial College were carried unanimously, the respective proposers and seconders being Principal S. SKINNER and Mr. S. D. CHALMERS, Mr. A. A. CAMPBELL SWINTON and Mr. D. OWEN, and Mr. W. DUDDELL and Mr. C. C. PATERSON.

Prince B. GALITZIN was balloted for and elected an Honorary Fellow of the Society.

The following is the list of officers elected for the ensuing year:—

*President*—Sir J. J. Thomson, O.M., D.Sc., F.R.S.

*Vice-Presidents* (who have filled the office of President)

—Prof. G. C. Foster, F.R.S., Prof. W. G. Adams, M.A., F.R.S., Prof. R. B. Clifton, M.A., F.R.S., Prof. A. W. Reinold, C.B., M.A., F.R.S., Prof. Sir Arthur W. Rucker, M.A., D.Sc., F.R.S., Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S., Prin. Sir Oliver J. Lodge, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S., R. T. Glazebrook, D.Sc., F.R.S., Prof. J. Perry, D.Sc., F.R.S., C. Chree, Sc.D., F.R.S., Prof. H. L. Callendar, M.A., F.R.S., Prof. A. Schuster, Ph.D., F.R.S.

*Vice-Presidents*—W. R. Cooper, M.A., B.Sc., A. Russell, M.A., D.Sc., F. E. Smith, R. S. Whipple.

*Secretaries*—S. W. J. Smith, M.A., D.Sc., F.R.S., W. Eccles, D.Sc.

*Foreign Secretary*—R. T. Glazebrook, D.Sc., F.R.S.

*Treasurer*—W. Duddell, F.R.S.

*Librarian*—S. W. J. Smith, M.A., D.Sc., F.R.S.

*Other Members of Council*—S. D. Chalmers, M.A., Prof. G. W. O. Howe, M.Sc., Prof. J. W. Nicholson, M.A., D.Sc., Major W. A. J. O'Meara, C.M.G., C. C. Paterson, C. E. S. Phillips, F.R.S.E., Prof. A. W. Porter, B.Sc., F.R.S., Prof. O. W. Richardson, M.A., D.Sc., F.R.S., Prof. the Hon. R. J. Strutt, F.R.S., W. E. Sumpner, D.Sc.

A paper entitled "A Galvanic Cell which Reverses its Polarity when Illuminated," was read by Mr. A. A. CAMPBELL SWINTON.

If two plates—one of zinc and the other of tinned copper coated on one surface with selenium and varnished with enamel over the remainder of its surface—are immersed in tap-water, the electric current through a galvanometer connected to the plates shows that in the dark the zinc is electro-positive to the selenium, while the result of light falling on the selenium is to increase the effect.

If, however, instead of zinc, carbon or copper is employed for the non coated plate, the interesting result is obtained that, while the selenium proves to be electro-positive to the carbon or copper in the dark, it immediately becomes electro-negative to carbon or copper the

moment it is illuminated, this being easily shown by the deflections of the galvanometer in contrary directions as the light is turned on and off.

#### DISCUSSION.

Prof. T. MATHER asked if the increase of current produced by the illumination was proportional to the E.M.F. which the author had detected with the quadrant electrometer.

Mr. S. D. CHALMERS asked if the heat waves would produce the effect.

Mr. W. DUDDALL commented on the fact that the visible rays were most effective while the ultra-violet rays were ineffective, and contrasted the result with the recent discovery that selenium is very sensitive to X-rays.

Mr. D. OWEN asked if the action was instantaneous. If so, by using intermittent illumination one should get a strong effect produced in a telephone circuit.

Mr. G. D. WEST thought that the ineffectiveness of the ultra-violet radiation might be due to the absorption of these rays which was bound to occur in the electrolyte.

The AUTHOR, in reply, said that the extreme instability of the cell made it impossible to co-ordinate readings of the current and the E.M.F. produced by illumination. He did not think heat waves were able to produce the effect, as passing the light through a solution of alum did not greatly reduce it. The action, he thought, was practically instantaneous. He agreed that the absorption of the cell would probably account for the ineffectiveness of the ultra-violet rays.

A paper entitled "*On the Criterion of Steel suitable for Permanent Magnets*," by Prof. S. P. THOMPSON, F.R.S., was read in abstract by the Secretary, the author not being present.

Whatever the form to be given to a permanent magnet, the prime requisites as to the quality of the steel are (1) large remanent magnetism ( $I_{rem.}$ ) and a high coercive (force  $H_c$ ). Since Hopkinson's determinations of 1885 it has been supposed that for the purpose of making permanent magnets the best material would be that for which both of these quantities and, consequently, their numerical product, should be as high as possible. Recently Mr. J. A. MATHEWS and, independently, Mr. J. R. ASHWORTH, have proposed to take the ratio  $H_c \div I_{rem.}$  or  $H_c \cdot I_{rem.}$  which only differs in sale as the criterion.

To decide as to the suggestion to take the ratio instead of the product a table giving the values of  $H_c \cdot I_{rem.}$ ,  $H_c \div I_{rem.}$  and  $H_c \times I_{rem.}$  for a number of steels is given, and it is clearly shown that the use of the ratio as a criterion of magnetic usefulness leads to most absurd results. As an example, annealed manganese steel (almost non-magnetic) should, judging from the ratio, be six times as good as Remy steel, whereas in reality, for equality of pull, a magnet of manganese steel would require to be 312 times the weight of that made of Remy steel. The qualities requisite in an ideal steel for permanent magnets are indicated.

#### DISCUSSION.

Dr. S. W. J. SMITH said that in cases (by far the most numerous) in which it was as essential that the moment of the magnet should be high as that it should be permanent, the criterion  $H_c \div I_r$  a maximum obviously had very little to be said for it in comparison with the criterion  $H_c \times I_r$  a maximum as Prof. Thompson had so clearly shown. It was possible, however, to think of cases where a "permanent magnet" might be required in which the constancy of the moment might be much more important than its magnitude. In these cases more might be said in favour of the first criterion. He pointed out that the choice between two different materials for a particular purpose might depend as much upon the shape of the  $IH$  curve as upon the values of  $I_r$  and  $H_c$ .

Mr. A. CAMPBELL said that for practical purposes it was important that  $I_r$  should be large or else a large coercive force was of no use. He agreed therefore that the pro-

duct of  $H_c$  and  $I_r$  was the most useful criterion, and could not think of a case where the quotient would give a useful indication of the quality of the steel.

Dr. C. CHREE said that peculiar cases were often encountered in which it was difficult to say exactly what interpretation should be put on the terms "permanent magnetism," "coercive force," &c. Some years ago he had had occasion to demagnetise a bar of cobalt. He had used the ordinary method of reversals, accelerating the process by hammering. By this process he actually reversed the magnetisation, a phenomenon which he attributed to the original magnetism being in the opposite direction in the outer layers to what it was in the inner core, the magnetism of the outer layers being destroyed by the hammering. He had also found with a certain dip needle that it could be magnetised more strongly in one direction than in the other. It was afterwards found that the steel from which the dip needle was made had been magnetised very strongly in that direction by the maker. There was another factor of importance besides the permanence of the moment of a magnet, and that was permanence of the distribution of the magnetisation. He cited the case of two Kew magnetometer magnets which had inadvertently been allowed to touch. Their moments were unaltered, but their mutual influence was considerably affected owing to a change in the distribution of the magnetisation.

Mr. E. H. RAYNER communicated the following:—From a practical point of view a high value for the product of remanence  $\times$  coercivity is to be desired with the proviso that a low value in one of them cannot compensate for a corresponding unusually high value in the other. A "figure of merit" might be made out by penalising the material in both of these properties, counting only after a certain value has been attained. This figure might be calculated from the formula  $(I_r - 400) \times (H - 20)$ . This would give a positive figure of merit to fifteen materials in the list given in the paper, implying that from a practical point of view the rest were comparatively worthless. The order of those with a positive figure of merit is much the same as the order of the magnitudes given in the last column of the paper, the first four being in the same order and the fifth and sixth inverted. The most notable exception is the molybdenum tungsten steel which comes tenth in order of merit in the last column of the paper, but which by reason of having a value for  $I_r$  of less than 400—namely, 370—has a negative figure of merit on the basis suggested. It would be interesting if Prof. Thompson could give some idea of what is the minimum value for  $H_c$ , which is desirable in a good permanent magnet for commercial purposes, such as magnetos for explosion engines.

A paper entitled "*An Investigation of the Photographic Effect of Recoil Atoms*," by Messrs. A. B. WOOD, M.Sc., and A. I. STEVEN, M.A., was taken as read.

The ionising, phosphorescent, and photographic effects of the  $\alpha$ -particles from a radio active substance entirely cease when the particle still retains about 40 per cent of its kinetic energy. It appears possible, therefore, that the recoil atoms from a radio-active source should be able to affect a photographic plate, for though the range of a recoil atom is only about 1/500th of that of the  $\alpha$ -particle shot off from it, the ionising effect has been shown by Wertenstein and one of the authors to be ten times as powerful over the corresponding range as that of the  $\alpha$ -particle.

Attempts have therefore been made to demonstrate this action in the case of the recoil atom from polonium, this substance being chosen on account of the inactive nature of the recoiling atom. Two distinct methods were employed: (1) The recoil atom was "absorbed"; (2) the difference of deflection of the  $\alpha$ -particle and the recoil atom in a strong magnetic field was utilised in order to attempt to separate their effects. "Schumann" plates were used as being most easily penetrable, but in all cases

the results were negative or inconclusive. This is probably due to the fact that the recoil atoms are not able to penetrate sufficiently deeply into the sensitive layer to render the grains developable.

## NOTICES OF BOOKS.

*Advanced Inorganic Chemistry.* By P. W. OSCROFT, M.A. (Cantab.). London: G. Bell and Sons, Ltd. 1915.

THIS book is intended to be used by young students who have had a year's course in theoretical and practical chemistry, or by older students who are beginning the study of the subject. In many respects it shows the characteristics of the work of the experienced teacher, and the practical exercises described are distinctly good; they include both preparations and analysis, and in addition many problems in calculation are included, many of them being taken from University Scholarship examinations. The profuse use of capital letters for the chemical and even some common names would hardly appear to be justifiable, and in matters of detail some of the author's statements are open to criticism; e.g., the assertion that "the detection of sodium is never certain" would be misleading, and the absence of all allusion to spectral analysis until the last chapter is regrettable.

*University of London Appointments Board. Its Aims and Work.*

THIS pamphlet describes the aims and work of the Board instituted by the University of London to assist graduates and students to obtain appointments. The value of a central office and information Bureau which has opportunities of keeping in touch with employers is obvious, and many appointments have been made through its instrumentality. As far as possible individual assistance is given to those who register, and the requirements and needs of business employers are taken into special consideration, while the Board is in direct communication with the similar Boards of other universities, and with Government Departments, Local Education authorities, and numerous public and private agencies at home and abroad.

*Bulletin of Armour Institute of Technology.* General Information Number. 1914.

THIS bulletin contains full information relating to the courses of instruction at the Armour Institute of Technology at Chicago. The equipment of the various laboratories is described in detail, and general information relating to entrance and other examinations, scholarships, &c., is given for the benefit of intending students. The Institute provides an opportunity for young men of all classes to obtain a sound technical education, especially in engineering. Much stress is laid on the necessity for the student to have a good grounding in general subjects before he enters upon his college course, and the curricula appear to be carefully planned and thoroughly practical in scope.

*Bulletin of Agricultural and Commercial Statistics.* Rome: International Institute of Agriculture.

THE February number of the "Bulletin of Agricultural and Commercial Statistics" issued by the International Institute of Agriculture publishes reports on the areas sown, and the condition of winter cereals in Northern Hemisphere countries. In countries for which there are data an increase is generally reported in the areas sown compared with last year, especially in India and the United States, which show increases of 22 and 11 per cent respectively. Regarding crop conditions, although the season has been exceptionally wet in many countries, no damage of notable importance is complained of as a

rule at present. In the current number of the Bulletin the good reports on the Southern Hemisphere wheat crop are confirmed, the production for the group comprising Argentina, Chili, Australia, and New Zealand being estimated for 1914-15 at 68,213,151 quintals compared with 64,154,155 in 1913-14, or 106.3 per cent. As for other products, there are shown the 1914-15 harvest data of cotton in India, viz., 8,981,131 quintals or 99.9 per cent of last year's production. The Bulletin next reproduces the tables with the production figures for cereals, flax, cotton, tobacco, vines, sugar-beet, and potatoes of 1913-14 in Northern Hemisphere countries, the data being modified according to the most recent official communications of final harvest data. The agricultural part of the Bulletin concludes with latest live-stock statistics for the United States and Costa Rica. In the commercial part the usual tables follow for imports and exports of cereals, linseed, and cotton, for visible stocks, and for prices of cereals and cotton on the world's principal markets, the tables being as complete as possible under present conditions.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 4, January 25, 1915.

This number contains no chemical matter.

*Bulletin de la Société Chimique de France.*

Vol. xv.-xvi., Nos. 16-20, 1914.

**Thermoregeneration of different Diastases of Yeast.**—Gabriel Bertrand and M. Rosenblatt.—When an aqueous maceration of dry yeast is examined it is found to contain not only sucrase but also analogous substances, among which the most abundant are maltase and catalase. The authors have found that neither the maltase nor catalase, like sucrase, gives rise to the phenomenon of thermoregeneration; that is to say, after their characteristic actions have been abolished by coagulation at, say, 80°, they cannot be regenerated by raising the temperature higher.

## MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Royal Institution, 3 "Colour Photography - Scientific Applications," by Prof. W. J. Pope, F.R.S.

WEDNESDAY, 10th.—Royal Society of Arts, 8. "Patent Law Reform and the War," by J. W. Gordon.

THURSDAY, 11th.—Royal Institution, 3. "Poetry and War," by Sir Herbert Warren, K.C.V.O.

— Royal Society of Arts, 4.30. "L'Evolution de l'Ecole Belge de Peinture (1830-1900)," by M. Paul Lambotte.

— Biochemical Society, 5.30. (In the Medical School of St. Bartholomew's Hospital).

— Royal Society. "Study of the Bionomics and Reproductive Processes of the Foraminifera," by E. Heron-Allen. "Occurrence of an Intercranial Ganglion upon the Oculomotor Nerve in *Scyllium canicula*, with a suggestion as to its bearing upon the Question of the Segmental Value of certain of the Cranial Nerves," by G. E. Nicholls. "Experiments on the Restoration of Paralyzed Muscles by means of Nerve Anastomosis—Part III., Anastomosis of the Brachial Plexus, with a consideration of the Distribution of its Roots," by R. Kennedy. "Mechanism of the Cardiac Values," by A. F. S. Kent.

FRIDAY, 12th.—Royal Institution, 9. "Back to Lister," by Sir Rickman J. Godlee.

— Physical, 8. "Estimation of High Temperatures by the Method of Colour Identity" and "Unit of Candle-power in White Light," by C. C. Paterson and B. F. Dudding. "Relative Losses in Dielectrics in Equivalent Electric Fields, Steady and Alternating (R.M.S.)," by G. L. Addenbrooke.

SATURDAY, 13th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

# THE CHEMICAL NEWS.

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## MICROSCOPIC TESTS ON OPAQUE MINERALS\*

By EVEREND L. BRUCE.

THE determination of opaque minerals when occurring as small grains in rocks, or when in intimate association in ores, is one of the difficult and uncertain problems of mineralogy. The translucent and transparent minerals yield to well known microscopic methods, but thus far few such tests have been devised for the opaque minerals. Considerable work has been done by different investigators, largely, however, with the purpose of ascertaining the paragenesis of known minerals rather than determining unknown ones. It is the purpose of this paper to combine the various tests devised by those who have worked along this line with a few additional methods that seem applicable to the problem, in an attempt to construct at least a partial determinative scheme.

Among the early articles on the subject is one by William Campbell (*Economic Geology*, ii., 350), giving the following distinguishing characteristics for the minerals studied:—

**Magnetite.**—Steel grey colour; polishes well; etches along parting planes, often yielding gridiron structure;  $H = 5\frac{1}{2}$  to  $6\frac{1}{2}$ .

**Chalcopyrite.**—Yellow colour; Polishes easily;  $H = 4$ .

**Pentlandite.**—Light bronze colour; polishes better than pyrrhotite; not so brittle; sometimes shows distinct cleavage; distinguished from pyrrhotite by etching;  $H = 4$ .

**Pyrite.**—Pale brass colour; polishes with difficulty; usually shows scratches; polishes in relief;  $H = 6$  to  $6\frac{1}{2}$ .

**Pyrrhotite.**—Light bronze colour similar to pentlandite; more brittle than pentlandite and shows a pitted surface;  $H = 4$ ; by immersing a specimen in hot HCl (1 : 1) pyrrhotite is attacked, while pentlandite is not.

Campbell and Knight used the method of polishing and etching on various cobalt ores, but no definite determinative tests are recorded.

Bastin, in his paper on metasomatism in sulphide enrichment, records the fact that polybasite with strong  $HNO_3$  is not etched so readily as chalcocite, but slowly exhibits a yellowish brown colour with a slight iridescence in places. Chalcopyrite similarly treated shows a faint peacock tarnish.

The most detailed work on the identification of opaque minerals is that of F. C. Lincoln. He has examined the gold ores and constructed the accompanying scheme for the determination of most of the several gold minerals (0 = no effect).

Etching by means of an electric current produced by a small platinum triangle has been tried by Beijerinck with the following results:—

**Cassiterite.**—Deposit of black metallic tin.

**Chalcopyrite.**—Becomes black.

**Pyrite and Pyrrhotite.**—Not affected.

In constructing a scheme from these tests and from others that were devised, the object aimed at was the determination of minute grains of mineral. This was not always successfully done. Some of the results depend on chemical reactions which it is as yet impossible to localise, and to that extent the results obtained are uncertain. A brief statement of the methods of preparation of the specimens and of obtaining the special results will be followed by a summary in schematic form.

**Preparation of the Specimen.**—The polishing of the mineral is fully described by Campbell in *Economic Geology* (i., 751), but for completeness a brief summary is given here. A fairly flat specimen is chosen if possible, and this is ground to a plane surface on a horizontally rotating iron lap, armed with medium grade carborundum. After a thorough washing the specimen is treated on a copper lap with No. 100 emery until the grooves of the coarse grinding are erased. This is followed by No. 200 emery until the scratches of the No. 100 powder disappear. In all cases the specimen is rotated to prevent unequal effect. After washing and drying the surface is polished on three grades of polishing paper, Nos. 0, 00, 000, mounted either on boards, the motion being produced by hand, or on wooden laps rotated as before. The grinding in each case is continued until the scratches from the previous treatment are removed. The orientation of the specimen in each succeeding treatment should be at right angles to that in the previous one, so that the scratches of the finer paper will be across those of the coarser. After polishing with the finest paper a lap covered with broadcloth saturated with rouge and water is used for the finishing process. By this means a high polish can be obtained.

**Instruments.**—The microscope used for this investigation was one with which both inclined and vertical illumination could be obtained. Inclined illumination was secured by a small parabolic mirror attached to the objective; vertical illumination by a movable glass disc in the barrel of the microscope. The source of light for ordinary work was a Welsbach lamp, the light being focussed by a plano-convex lens. For some minerals the light was filtered through a flask of copper sulphate solution, replacing the lens; by this means light containing no yellow rays can be obtained. For applying chemicals to the polished surface small glass tubes drawn to a fine point are useful. For physical tests any small fine-pointed instrument can be used.

**Methods.**—The mineral, prepared as above described, was first examined for colour and appearance. For this purpose obliquely incident light gives the best results. Following this one large specimen was broken into several smaller ones, some of which were treated further, while one was kept for reference. Etching was first tried with strong cold HCl, at half-minute intervals or less, if much action took place. If unattacked after a reasonable time strong cold nitric acid was substituted for the hydrochloric. Finally, aqua regia was used with substances that resisted both single acids.

In the case of minerals that behaved in the same manner under etching, special chemical or physical tests were tried. In chemical tests the grain to be tested was brought into focus under a fairly low-power objective, and touched with an acid capable of etching it. After the action had continued for a short time a drop of a reagent producing characteristic reactions was added. Under the microscope only very small quantities are necessary, and with care rather small grains can be thus tested. The chief reactions employed are the following:—

1. **Iron.**—The grain touched with freshly prepared mixture of potassium ferrocyanide and acid becomes deep blue if iron be present.

2. **Nickel.**—The mineral is treated with a mixture of  $HNO_3$  and tartaric acids. After evaporation, when touched with a solution of dimethylglyoxime freshly made ammoniacal, a brilliant red is obtained from minerals carrying nickel.

3. **Copper.**—In the presence of copper a mixture of  $HNO_3$  and potassium ferrocyanide solution gives a deep red. If iron also be present this is followed by green.

4. **Manganese.**—Most manganese minerals are attacked by HCl with production of a deep brown solution which becomes colourless on addition of hydrogen peroxide.

5. **Silver.**—The mineral is treated with nitric acid. Addition of hydrochloric acid produces a white precipitate. Also true of lead and mercury minerals.



Mineral	Colour.	Texture.	HNO <sub>3</sub> (1:1).	HNO <sub>3</sub> (1:2).	HNO <sub>3</sub> (1:4).	HCl (1:1).	With Hg.
Gold ..	Deep yellow.	Smooth.	o	o	o	o	Amalg.
Chalcopyrite..	Deep yellow.	Rough.	o	o	o	o	o
Pyrite ..	Pale yellow.	Slightly rough.	Black tarn.	Black tarn.	o	o	o
Marcasite ..	Pale yellow.	Slightly rough.	Black tarn.	Black tarn.	o	o	o
Pyrrhotite ..	Pale reddish yellow.	Very rough.	o	o	o	o	o
Calaverite ..	Pale yellow.	Smooth.	Bronze tarn.	Bronze tarn.	o	o	o
Sylvanite ..	Pale yellow.	Smooth.	Bronze tarn.	Bronze tarn.	o	o	o
Nagyagite ..	White.	Smooth.	Grey tarn.	o	o	o	o
Petzite ..	White.	Smooth.	Brown and blue } tarn.	Brown and blue } tarn.	o	Grey tarn.	o
Hessite ..	White.	Smooth.			o	Grey tarn.	o
Galenite ..	White.	Smooth.			Brown and blue tarn.	Grey tarn.	o

6. *Bismuth*.—The mineral is touched with nitric acid, followed, after drying, by hydrochloric. A little water will then produce a white precipitate.

*Physical Tests*.—In a few cases streak and hardness are useful. These tests can be made with a needle point.

Besides the above a few other tests were tried. Deposition of silver from weak silver sulphate solutions by certain minerals may possibly be useful as a criterion. An experiment was tried with marcasite and pyrite in a 10 per cent solution. What seemed to be a dendritic growth of silver formed on the marcasite after long immersion, while the pyrite remained bright and unchanged. Further tests with variation of temperature and concentration are necessary, however. The rate of attack in the process of etching is also sometimes a valuable aid in identification.

The scheme outlined below depends for its major division on the colour of the polished mineral. In each colour division subdivisions are made by etching tests. Special behaviour of different minerals makes further differentiation possible in many cases.

#### I. MINERAL BY INCLINED ILLUMINATION IS YELLOW.

##### A. Etched by HCl.

*Pyrrhotite*.—Bronzy yellow; surface rough; reacts for Fe.

##### B. Etched by HNO<sub>3</sub>, not by HCl.

##### (a) Without noticeable tarnish or deposit.

*Pyrite*.—Pale yellow; slightly rough; reacts for Fe.  
*Marcasite*.—Pale yellow; slightly rough; reacts for Fe; precipitates Ag (?).  
*Millerite*.—Slightly rough; reacts for Ni.

##### (b) With tarnish.

*Chalcopyrite*.—Deep yellow; rough; reacts for Fe and Cu; iridescent tarnish.

##### C. Not attacked by Single Acids.

*Gold*.—Deep yellow; smooth; amalgamates with Hg.

#### II. MINERAL IS WHITE.

##### A. Etched by HCl.

##### B. Etched by HNO<sub>3</sub>.

##### (a) With no tarnish or deposit.

*Smaltite*.—Rough with bright facets; gives Ni test.  
*Arsenopyrite*.—Rough with bright facets; becomes grey with reddish spots; reacts for Fe, not for Ni.  
*Leucopyrite*.—White; very rough; reacts for Fe.  
*Silver*.—Smooth; reacts for Ag.  
*Bismuth*.—Smooth; reacts for Bi.

##### b) With deposit.

*Arsenic*.—Chalky white deposit.  
*Antimony*.—Chalky white deposit.

##### C. Unattacked by Single Cold Acids.

*Cobaltite*.—Slightly rough; etched by HNO<sub>3</sub>.

*Nickolite*.—Slightly rough with reddish tinge; treated with aqua regia reacts for Ni.

#### III. MINERAL IS BLACK OR GREYISH BLACK.

##### A. Etched by HCl.

*Magnetite*.—Shows intersecting parting planes; etches easily; Fe reaction.

*Franklinite*.—Fairly smooth; etches less readily than magnetite.

*Ilmenite*.—Fairly smooth; etches very slowly.

*Hæmatite*.—Steel-grey; smooth; red streak.

*Manganite*.—Dull black; brown solution.

*Psilomelane*.—Brown and black areas; brown solution.

*Braunite*.—Black; etches to bluish black; brown solution.

*Alabandite*.—Smooth greyish black; very easily attacked (40 sec.).

*Pyrolusite*.—Black fibrous surface; soft brown solution.

##### B. Etched by HNO<sub>3</sub>, not by HCl.

##### (a) Without tarnish.

*Enargite*.—Dull greyish black; etches to fibrous structure; Cu test.

*Argentite*.—Smooth dull black; Ag test; sectile.

*Stephanite*.—Smooth dull black; Ag test.

##### (b) With a tarnish.

*Chalcocite*.—Smooth black; etched to a bluish tarnish, later becoming peacock colours.

*Bornite*.—Pitted; purple colour; etches to a peacock tarnish; reacts for both Fe and Cu.

##### (c) With a deposit.

*Galenite*.—Smooth black; etches easily, with a yellow deposit.

*Bournonite*.—Smooth dull black; etches easily, with yellowish opalescent deposit; Cu test.

*Stibnite*.—Smooth dull black; etches fairly slowly to a fibrous structure with a chalky deposit.

*Tetrahedrite*.—Smooth; bluish black; etches with an opalescent deposit; reacts for Cu.

##### C. Unattacked by Single Acids.

*Molybdenite*.

*Chromite*.

*Cassiterite*.—Black deposit by electric etching.

*Columbite*.

The table as presented is by no means complete, and some of the minerals treated cannot be absolutely determined by the tests recorded, but it is believed that the compilation of what is known will be of distinct advantage.

In conclusion, the writer wishes to acknowledge the advice and assistance of Prof. A. J. Moses in the work upon which this article is based.—*School of Mines Quarterly*, xxxv., No 3.

# HYDROGEN : ITS TECHNICAL PRODUCTION AND USES.

By A. F. SEEKER.

IN recent years the cheap production of hydrogen on a large scale for technical purposes has become a problem of some importance. Formerly it was used occasionally for filling balloons and in the oxy-hydrogen flame of the so-called "calcium light." Being the lightest of the common gases and of a correspondingly high sustaining power, it has become essential for the filling of dirigible balloons with their heavy burden of propelling machinery. Such uses, however, have become of rather secondary importance, and it will probably be only a short time before the dirigible balloon and the "calcium light" will have been permanently discarded in favour of heavier than air machines and the varied forms of projected lights operated by electricity.

The oxy-hydrogen flame is now becoming a common tool in the hands of the artisan in working refractory metals; liquid oils and soft greases are now "hydrogenated" to produce acceptable lard and butter substitutes, and also solid fat suitable for the manufacture of hard soaps; and lastly, the use of which promises to consume enormous quantities, ammonia is manufactured from hydrogen and atmospheric nitrogen. All these uses tend to make the problem of the production of cheap hydrogen one of considerable importance.

The employment of the oxy-hydrogen torch is too well known to require description here. The commercial "hydrogenation" of oils and fats is of recent introduction. The process consists in treating the oil or grease in a suitable vessel containing a catalysing agent, generally nickel, with hydrogen under pressure. The oil is violently agitated in order to bring it into intimate contact with the hydrogen and catalyser. The result is that the glycerol esters for the unsaturated fatty acids, which generally consist for the most part of oleic acid, become saturated, and the mono-, di-, or triolein, as the case may be, is converted into the corresponding stearin. The oleins are either liquid or semi-solid at ordinary temperature, and produce soft soap or soap that will not hold much water without becoming soft. The stearins are solid fats at ordinary temperatures and produce hard soaps. Thus by the process of hydrogenation, cotton seed and corn oils are to-day being converted into lard and butter substitutes, and the soft waste grease which formerly could only be used sparingly in soap on account of their softening effect can now be employed alone as soap stock. The importance of this is understood when the constantly soaring prices of animal tallow are taken into consideration.

In view of the impending exhaustion of the Chili nitre beds, the problem of the fixation of atmospheric nitrogen for the manufacture of artificial fertilisers has received constantly increased attention. Electrical methods for the production of cyanamid from calcium carbide and nitrogen, and the flaming arc process for making nitric acid directly from the air, have been established upon a successful commercial footing, but these require such an enormous expenditure of energy that they can only be operated profitably where there is an abundance of cheap water power. If only these processes were available, countries lacking in water power would be placed at a distinct disadvantage, and for this reason many chemists, particularly those of Germany, have laboured to find a process better suited to the conditions surrounding them. The details of this search were described in a most interesting manner before the Eighth International Congress of Applied Chemistry, by Hofrat Dr. H. A. Bernthsen, who is the Chemical Director of the Badische Anilin und Soda Fabrik, the owners of a synthetic ammonia factory now in successful operation at Oppau, near Ludwigshafen on the Rhine.

The process, which has been named after Haber, its inventor, consists in passing a mixture of pure nitrogen and

hydrogen under a pressure of 150 to 250 atmospheres through a tube filled with a catalyst and heated to 650 to 700° C. The hot gases then pass through a heat regenerator and thence through an ammonia absorber, after which they are replenished with fresh gas mixture and forced by a pump back over the outer walls of the contact tube and then through the contact mass to repeat the circulatory course already described. Only a part of the gas mixture is converted into ammonia by a single passage through the converter, but the gases are made to circulate continuously through the apparatus, the ammonia being absorbed each time as the mixture issues from the heat regenerator at the end of the contact tube. The gases are replenished with fresh hydrogen-nitrogen mixture as required. The contact mass consists of pure iron containing small amounts of certain so-called promoters which may consist of oxides, hydroxides, or salts of the alkalis or of the alkaline earths, and also many other substances of the most varied nature, especially metallic compounds or the metals themselves.

There have been many ways proposed for the producing of hydrogen on a large scale, the most important of which are the electrolytic and the water gas process. The studies of A. Wegener and others lead to the belief that at an altitude of about 75 miles the atmosphere consists of pure hydrogen and nitrogen that would be ideal for the Haber process. Unfortunately no means of piping these gases down to our sphere of action are known and we must content ourselves with more laborious methods of production.

At European army posts, hydrogen for military balloons is commonly generated from scrap iron and sulphuric acid, the reaction being accelerated by heating the mixture to about 55° C. For field operations zinc is used in place of iron and the generators are mounted on wheels to facilitate transportation. Three other, and more modern means, of generating hydrogen are used for field purposes and will no doubt be adapted for other than military uses in places difficult of access where the gas is needed. These processes were invented by G. F. Jaubert, a Frenchman, and were named by him respectively, the "Hydrolith," "Silicol," and "Hydrogenite" processes.

Hydrolith is formed by heating metallic calcium in an atmosphere of hydrogen, producing a hydride,  $\text{CaH}_2$ , which when treated with water reacts as follows— $\text{CaH}_2 + \text{H}_2\text{O} = \text{Ca(OH)}_2 + 2\text{H}_2$ , just as calcium carbide generated acetylene. Hydrolith is a white crystalline powder, decomposing at 600 degrees in a vacuum, and usually contains about 90 per cent of  $\text{CaH}_2$ , the rest being nitride and oxide. One kilogram yields about 1 cm. of hydrogen. The apparatus designed for using hydrolith in the French army is very ingenious, can readily be transported, and has a capacity of 1200 cm. per hour. An army dirigible can be filled in four hours. The high cost of hydrolith, 1.33 dols. per kilogram, will at present seriously restrict its use outside of military operations.

The Silicol process consists in treating powdered ferrosilicon, or mangano-silicon with water and caustic soda. It does not appear to have gained extended use because of the more troublesome manipulations and the greater difficulty of controlling the evolution of gas as compared with the other methods.

Hydrogenite is composed of ferrosilicon (containing 90 to 95 per cent of metallic silicon) 25 parts, caustic soda 60 parts, and dry slaked lime 20 parts. The ingredients are reduced to a very fine powder, intimately mixed, and pressed into brick weighing 25 to 50 kilograms. Being very hygroscopic, each brick must be sealed in a tin box to prevent decomposition. In generating hydrogen the brick is placed in a metal chamber having double walls, the space between the two walls being filled with water. Vents are placed in the upper part of the inner wall leading to the central chamber containing the hydrogenite so that the steam formed during the combustion may gain access to the charge and increase the yield. The cover of the tin containing the hydrogenite is opened, the tightly

fitting lid of the generator fastened in place and through a small hole in the latter a red hot wire is thrust into the charge. The mass burns quickly, without flame, generating heat and evolving hydrogen according to the equation  $\text{Si} + \text{Ca}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2\text{SiO}_3 + \text{CaO} + 2\text{H}_2$ . One volume of the compressed hydrogenite yields 800 volumes, or 270 to 370 litres per kilogram, of pure hydrogen, at a cost of about 32 cents per cubic metre. The requisite apparatus for field purposes weighs about 900 kilograms.

The methods employed upon a large scale are, of course, capable of producing the gas much more cheaply. In one of these an iron, clay-lined retort is filled seven-eighths full of coke, ignited and raised to a white heat by an air blast. The retort is then closed and a cheap hydrocarbon like crude petroleum or coal-tar is injected into it from the top for about twenty minutes or until the temperature has fallen below the proper cracking point, the gas thus generated passing through a sprinkling tower and filtered into the gasometer. The oil injector is then shut off, the retort opened, the air-blast again turned on, and the process repeated indefinitely with periodical renewal of the coke and removal of the ashes. The product contains about 2.7 per cent  $\text{CO}$ , 95.0 per cent  $\text{H}$ , and 1.3 per cent  $\text{N}$ , and has a specific gravity of 0.1. The gas can be still further purified to a content of 98.4 per cent  $\text{H}$ , by passing it through suitable absorbents, and is produced at a total cost of 3 to 4 cents per cubic metre, according to the size of the plant and the materials used.

Large amounts of hydrogen are obtained as a by-product in the electrolysis of salt solutions in the manufacture of chlorine and of caustic soda. The electrolysis is effected in a cell having a cement diaphragm which is not attacked by chlorine or caustic soda. The electrodes are iron and carbon, the latter being used as an anode. The reaction, which is as follows— $2\text{NaCl} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{Cl}_2 + \text{H}_2$ , yields 7000 cubic feet of hydrogen for every ton of salt. A cell operates on 15,000 horse-power at Griesheim, Germany, producing 245 million cubic feet of hydrogen per annum.

Two other methods, now little used, consist, (1) in passing superheated steam over red-hot iron, and (2) in conducting water-gas through suitable absorbents so that the carbon-monoxide and hydrocarbons are removed, leaving behind the hydrogen and nitrogen. A third process which is increasing in application was devised by Linde, Frank, and Caro. In this, water-gas which consists mainly of carbon monoxide and hydrogen is compressed and cooled to the liquefying point of the carbon monoxide. Upon relieving the pressure the mixture expands and in so doing is cooled still further so that the carbon monoxide and most of the impurities separate out in liquid form, allowing the hydrogen to pass off in a fairly clean (97 to 98 per cent  $\text{H}$ ) condition. The mixture containing the liquid carbon monoxide is later vaporised and used in combustion motors for power.

The growing demand for cheap hydrogen for industrial uses will act to promote improvements in both the electrolytic and the water-gas processes because both require comparatively cheap raw material. The former will probably be favoured in districts having abundant water power, whereas the latter requires cheap coal as an initial factor. In any event the extensive growth of the field of application will furnish sufficient incentive for the determination of still more economical processes than now exist.—*The Chemical Engineer*, xx., No. 6.

Royal Institution.—On Tuesday next, March 16, at 3 o'clock, Prof. Sir J. G. Frazer will begin a course of two lectures at the Royal Institution on "The Belief in Immortality among the Polynesians"; and on Thursday, March 18, Dr. Aubrey Strahan will commence a course of two lectures on "London Geology." The Friday Evening Discourse on March 19 will be delivered by Prof. G. H. Bryan, on "The Modern Piano Player—Scientific Aspects," and on March 26, by Prof. Sir J. J. Thomson on "Experiments in Slow Cathode Rays."

## THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.\*

By O. L. BARNEBEY.

(Continued from p. 116).

### Manganese Solutions with and without Phosphoric Acid (continued).

A SERIES of analyses was made using manganese chloride solution as preventive, thus eliminating sulphates and phosphates entirely. While the end-points were obscure on account of colour of the solution, nevertheless comparatively good results were obtained, showing good prevention. In this series (VIII.) the following solutions were used:—A ferrous chloride solution made by dissolving approximately 25 grms. of the crystallised salt in a litre of water containing 10 cc. of hydrochloric acid (sp. gr. 1.2); a manganese chloride solution containing 75 grms. of crystallised salt and 20 cc. of hydrochloric acid (sp. gr. 1.2) per litre; hydrochloric acid, sp. gr. 1.1. All the titrations were performed somewhat slower than usual, about two minutes being required for each titration.

TABLE VI.

Series VII.—Titration without  $\text{H}_3\text{PO}_4$ . 1 cc.  $\text{KMnO}_4 = 0.004396$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.2092$  gm. Fe) + 10 cc.  $\text{HgCl}_2$  taken.

Expt. No.	HCl. Cc.	Manganese solution No. 3. Cc.	Weight of Fe found.
1.	5	1	0.2123
2.	5	2	0.2112
3.	5	3	0.2105
4.	5	4	0.2098
5.	5	5	0.2101 (b)
6.	5	6	0.2098
7.	5	6	0.2096
8.	5	6	0.2096
9.	5	7	0.2092
10.	5	8	0.2092
11.	10	5	0.2105
12.	10	10	0.2092 (c)
13.	10	10	0.2101 (b)
14.	10	15	0.2092
15.	10	15 (a)	0.2092
16.	10	25	0.2090
17.	20	20	0.2090
18.	20	20	0.2092
19.	20	20 (a)	0.2092
20.	40	—	0.2180
21.	40	20	0.2096 (d)
22.	50	20 (a)	0.2096 (d)

(a) Manganese solution No. 1.

(b) Rather heavy  $\text{HgCl}_2$ .

(c) Light  $\text{HgCl}_2$ .

(d) Very slow titration.

### Application of other "Preventives."

The rôle which manganese salts play in preventing the action of hydrochloric acid on the permanganate in titration seemed to warrant a study of other substances to ascertain their action toward prevention.

The first class of substances tried were neutral salts. Skrabal (16) has studied the influence of the addition of varying amounts of normal neutral salt solutions in the titration of iron, arriving at the conclusion that these salts do not produce correct results. In this work much stronger solutions are employed, which accounts for somewhat different results. Sodium silicate, borate, and tetraborate give some prevention, but the adjustment between the amount of salt and acid to be used was too difficult to give any merit to the procedure. If too much silicate is used,

\* From the *Journal of the American Chemical Society*, xxxvi, No. 7.

the ferrous iron precipitates, and if too much sulphuric acid is added the end-point is indistinct—over-titration resulting. Sodium sulphate, when used in large enough amounts, gives a good titration. Potassium sulphate is not as effective, probably because of its limited solubility in water. Ammonium sulphate also prevents moderately well with low concentrations of hydrochloric acid and high concentrations of the ammonium salt, but is not as satisfactory as the former two. These observations are in contradiction to the work of Birch (23), who says that sodium sulphate and magnesium sulphate do not prevent, and that ammonium sulphate is worse than worthless.

TABLE VII.

Series VIII.—Manganese Chloride as Preventive. 1 cc.  $\text{KMnO}_4 = 0.004836$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.1717$  gm. Fe) + 5 cc. HCl taken.

MnCl <sub>2</sub> . Cc.	Manganese solu- tion No. 1. Cc.	Weight of Fe found.
—	20	0.1717
—	20	0.1717
—	—	0.1755
1	—	0.1745
2	—	0.1743
3	—	0.1740
4	—	0.1740
5	—	0.1732
6	—	0.1734
7	—	0.1729
8	—	0.1732
10	—	0.1722
12	—	0.1722
16	—	0.1724
20	—	0.1722
25	—	0.1722
50	—	0.1719
50	—	0.1719
50	—	0.1722
100	—	0.1722
100	—	0.1719
200	—	0.1719

TABLE VIII.

Series IX.— $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (250 grms. in litre) as Preventive. 1 cc.  $\text{KMnO}_4 = 0.004887$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.1930$  gm. Fe) + 10 cc.  $\text{HgCl}_2$  taken.

Expt. No.	HCl. Cc.	$\text{Na}_2\text{SO}_4$ . Cc.	Weight of Fe found.
1.	25	180	0.1961
2.	25	200	0.1961
3.	25	200	0.1956
4.	25	300	0.1937
5.	25	400	0.1930
6.	25	400	0.1930
7.	25	400	0.1930
8.	5	20 (a)	0.1930

Series X.— $\text{K}_2\text{SO}_4$  as Preventive. 1 cc.  $\text{KMnO}_4 = 0.004887$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.2290$  gm. Fe) + 10 cc.  $\text{HgCl}_2$  taken.

Expt. No.	HCl. Cc.	$\text{HgCl}_2$ . Cc.	$\text{K}_2\text{SO}_4$ . Cc.	Weight of Fe found.
1.	5	10	50	0.2297
2.	5	10	50	0.2297
3.	10	10	50	0.2312
4.	15	10	50	0.2331
5.	10	10	100	0.2299
6.	15	10	100	0.2301
7.	20	10	100	0.2326
8.	25	10	200	0.2306
9.	25	10	200	0.2304
10.	5	10	20 (a)	0.2290

(a) Mn solution No. 1.

Another series of results was obtained preceding this series, in which was used a supersaturated solution of sodium sulphate of about twice the strength of the one here employed. A correspondingly less volume of the sulphate solution was necessary for prevention.

In Series X. are tabulated the results obtained using a saturated solution of potassium sulphate, and from these results it is evident that potassium sulphate solutions do not contain sufficient alkali sulphate for good preventive purposes.

Cady and Ruediger (9) have published a method using mercuric sulphate as reagent to stop the influence of hydrochloric acid. To study the action of this reagent, 300 grms. of mercuric sulphate was dissolved in 1400 cc. of water containing 125 cc. of sulphuric acid (sp. gr. 1.84) and the solution applied in Series XI.

TABLE IX.

Series XI.—Mercuric Sulphate as Preventive. 1 cc.  $\text{KMnO}_4 = 0.004837$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.2150$  gm. Fe) + 5 cc. HCl taken.

Expt. No.	$\text{HgCl}_2$ . Cc.	$\text{HgSO}_4$ . Cc.	Manganese solu- tion No. 1. Cc.	Weight of Fe found.
1.	10	10	—	0.2118
2.	—	10	—	0.2167 (a)
3.	—	15	—	0.2155
4.	10	20	—	0.2167 (a)
5.	10	25	—	0.2150
6.	—	25	—	0.2150
7.	—	25	—	0.2155
8.	—	35	—	0.2228 (b)
9.	10	50	—	0.2297 (b)
10.	10	50	—	0.2297 (b)
11.	10	—	20	0.2150

(a) Indefinite.

(b) Very indefinite.

TABLE X.

Series XII.—Potassium and Sodium Acid Sulphates as Preventives. 1 cc.  $\text{KMnO}_4 = 0.004887$  gm. Fe. 20 cc.  $\text{FeCl}_2 (= 0.1596$  gm. Fe) + 10 cc.  $\text{HgCl}_2$  taken.  $\text{KHSO}_4$  = saturated solution.

Expt. No.	HCl. Cc.	$\text{H}_2\text{SO}_4$ . Cc.	$\text{KHSO}_4$ . Cc.	Weight of Fe found.
1.	5	—	—	0.1671 (a)
2.	5	25	—	0.1618
3.	5	—	25	0.1603
4.	5	—	25	0.1603
5.	5	—	50	0.1598
6.	5	—	50	0.1596
7.	5	25	50	0.1613
8.	5	50	50	0.1637
9.	10	—	25	0.1681 (a)
10.	10	—	50	0.1600
11.	15	—	50	0.1623
12.	15	—	75	0.1600
13.	20	—	100	0.1613
14.	20	—	125	0.1618
15.	20	—	150	0.1618
16.	20	—	175	0.1628
17.	20	—	200	0.1637
18.	20	—	500	0.1630
19.	5	—	100	0.1596
20.	5	—	100	0.1598

$\text{NaHSO}_4$  = 500 grms. per Litre.

Expt. No.	HCl. Cc.	$\text{HgCl}_2$ . Cc.	$\text{KHSO}_4$ . Cc.	Weight of Fe found.
1.	5	—	25	0.1598
2.	10	—	25	0.1613
3.	10	—	50	0.1603
4.	15	—	50	0.1625
5.	15	—	75	0.1620
6.	15	—	100	0.1623
7.	5	—	20 (b)	0.1596

(a)  $\text{HgCl}_2$  disappeared.

(b) Mn solution No. 1.

Results 1 to 4 inclusive show incomplete prevention, due to an insufficient quantity of mercuric sulphate. Experiments 5 and 6 were satisfactory. The results obtained in Experiments 8 to 10 inclusive were decidedly high, due apparently to the transposition of mercurous chloride to mercurous sulphate by the mercuric sulphate. This point is mentioned in Cady and Ruediger's (9) original paper. The difficulty of adjustment of the quantity of mercuric sulphate to the other variables of an iron determination reduces the value of such a reagent as mercuric sulphate.

Sodium acid sulphate and potassium acid sulphate prevent quite well when the quantity of hydrochloric acid to be counteracted is small. With larger amounts of hydrochloric acid, or in the presence of sulphuric acid with the smaller quantities of hydrochloric acid, results are not as good.

Experiments 5 and 6 indicate that about 50 cc. of 50 per cent potassium acid sulphate solution is necessary to stop the detrimental influence of 5 cc. of hydrochloric acid. Experiments 7 and 8 show higher titration results with sulphuric acid than without it. Nos. 19 and 20 indicate that an excess of the potassium acid sulphate does not give a higher value if the amount of hydrochloric acid remains the same. However, in Nos. 13 to 18 inclusive, in which the amount of acid was 20 cc., the potassium bisulphate gave a progressively higher titration as its concentration was increased. Sodium acid sulphate showed somewhat the same kind of deportment. These acid sulphates, while possessing preventive powers, do not have this quality to a sufficient degree to make them suitable for an accurate titration of iron.

(To be continued).

## THE SULPHATE IN RIVER WATERS.

By H. S. SHELTON.

MR. DOLE's recent remarks (CHEMICAL NEWS, 1915, cxi., 86) call for a brief reply. It is unfortunate that he has little to say on the scientific side and devotes his attention to copious quotations which prove nothing. In the main his remarks answer themselves. The suggestion that he has been misquoted is answered by his own quotations. The only quotation I made consists of thirteen words, which are repeated with absolute accuracy. Nor is the suggestion of misrepresentation much more sensible. When I assert that a certain part of the procedure in Mr. Dole's method of river water analysis is the principal difference between his method and Wanklyn's it is obvious that I am neither describing nor attempting to describe the procedure in full. The point that requires emphasis is that there is no attempt to reply to any suggestion made by me in either paper (CHEMICAL NEWS, cli., 75; cx., 307) and very little that has any bearing on the subject.

The small amount of relevant matter can be answered in a few words. Mr. Dole states that the product of evaporation of river water is sometimes carbonised. In such cases (there is no indication of their frequency) anything precipitated with the sulphate cannot be organosilicate, though it may be other complex silicates. Nothing, however, can be made of a vague statement of that kind. Also, in cases when the water-bath is heated by steam from the basement, the error cannot be due to fumes from the Bunsen burner. But, once again, the frequency is uncertain, and the statement is too vague to be of value.

Mr. Dole appears to doubt that fumes from the Bunsen burner can be an appreciable source of error when 10 to 15 mg. of barium sulphate are weighed. If he will read the paper to which I referred (*Journ. Chem. Soc.*, 1889, 545), and Warington's other papers, he will discover that such is approximately the quantity that Warington was accustomed to weigh. The suggestion that a smaller weight will give a result of any value is obviously absurd.

Nor did I think that any competent water analyst would dispute either Warington's authority or the statement that gas fumes are a very likely source of error. Plenty of evidence is available if the statement is seriously disputed.

With regard to Mr. Dole's last paragraph and his concern for the reputation for accuracy of the U.S.A. Geological Survey analyses, it is perhaps as well to say that there is no suggestion that such analyses are either more or less accurate than those of anyone else. The reputation for accuracy is not, however, enhanced by accusations of misquotation which are answered in his own paper, nor by the obvious indications that he has failed to grasp the arguments of the paper he is criticising. I refer to his suggestion that I take into account the solubility of sulphur compounds. If he will refer to my original paper he will find that I proceeded on the assumption that all the eroded sulphur compounds were dissolved and that no sulphur was carried to the sea in sediment.

## THE IDENTIFICATION OF ARTIFICIAL SILKS.

By LOUIS J. MATOS, Ph.D.

OWING to the constantly increasing use of artificial silks and the consequent confusion arising in dye-houses and silk mills generally, due to the occasional, though unintentional, mixing of lots, it becomes a matter of some importance for the dyer or manager to be able to identify with certainty the several important kinds of artificial silks on the market. Where a dyer goes on from day to day with his work, and on one kind of silk, it is a matter of some consequence when he finds himself confronted with the problem of dyeing a new lot of different kinds of silk that does not come out as expected, or which seems to offer difficulties during the dyeing.

Many instances are familiar to dyers where lots of mixed artificial silk have been sent to the dye-house, and inequality in the dyeing was not discovered until near the end of the operation, when it became a matter of great skill to bring up the shade of the indifferent skeins to the shade of the main lot. This condition could have been anticipated had the dyer been acquainted with the fact that the entire lot of silk was not of one kind.

From time to time there have been published tests and reactions with chemicals to be used in distinguishing the several kinds of artificial silks, but the practical application of which, in the dye-house or office, seems to offer some obstacles in the hands of those not actually acquainted with the details of making reactions. It seems that while the method of making the tests is simple enough the greatest difficulty is in having the solutions or reagents properly compounded and in conducting the tests afterwards.

Simple descriptions alone do not seem to meet the case entirely. Of course, there is nothing to take the place of a practical demonstration of a testing method when carried out by one who is practically familiar with the proper sequence of the operations. On the other hand, many of the methods for fibre testing that have been published, while apparently intended for dyers and practical mill men, being those most concerned, are, as a rule, written for the chemist with some experience, as only such could possibly have the unusual reagents and apparatus, or even the apparently delicate manipulative skill, to handle both satisfactorily.

Without question, the most satisfactory means to identify artificial silk is to make use of the microscope, but as very few mills are equipped with this valuable instrument, and fewer still are proficient in making use of it, we will omit its discussion as applied to artificial silk, and confine ourselves exclusively to the chemical or wet methods that experience has taught us as being the most satisfactory. To identify artificial silk properly requires that the person attempting the work should have



at hand a small set of chemical reagent bottles of not more than two-ounce capacity, and with glass stoppers. Such bottles are not costly, and may be obtained through a local druggist; the style known as "XX Tinctures" are admirably suited for the purpose. They are to be filled with the following reagents, which can be procured from a chemical supply house, or prepared by a friendly pharmacist or chemical friend. The following constitutes the list and the methods for their preparation:—

No. 1. *Glycerinated Sulphuric Acid.*

Pure glycerin .. .. .	10 cc.
Distilled water .. .. .	5 cc.

Add slowly with constant stirring, a few drops at a time, pure concentrated sulphuric acid—15 cc.

No. 2. *Iodo iodide of Potassium.*

Distilled water .. .. .	30 cc.
Potassium iodide .. .. .	0.3 gm.
Iodide, an excess.	

No. 3. *Chloriodide of Zinc.*

Distilled water .. .. .	30 cc.
Fused chloride of zinc .. .	1.75 gm.

Filter and add to clear filtrate iodine to saturation.

No. 4. *Cold Concentrated Sulphuric Acid.*

No. 5. *Half Saturated Chromic Acid.*

No. 6. *A 40 per cent Caustic Potash Solution.*

No. 7. *Copper Oxide Ammonia.*

This is an important reagent in all fibre work. It should be made with great care by preparing a solution of copper oxide in ammonia to saturation, and passing through it a current of air freed from carbon dioxide, by first being passed through a solution of caustic potash.

No. 8. *Nickel Oxide Ammonia.*

Nickel sulphate in crystals ..	2 gm.
Water .. .. .	30 cc.

Precipitate the nickel with caustic soda, and filter; then dissolve the precipitate in a mixture of:—

Concentrated ammonia .. ..	8 cc.
Water .. .. .	8 cc.

No. 9. *Alkaline Copper Glycerine Solution.*

Sulphate of copper .. .. .	3 gm.
Water .. .. .	30 cc.
Glycerin .. .. .	1.75 gm.

to which is added a sufficient quantity of caustic potash solution to precipitate the copper and re-dissolve it.

No. 10. *Diphenylamine Sulphuric Acid Solution.*

Diphenylamine .. .. .	1.57 gm.
Concentrated sulphuric acid ..	25 cc.

The operator should keep these bottles in a closet when not in use, and at all times free from dust. The label, besides the name, should also have the formula written upon it.

The apparatus required to make the tests consists of a dozen small plain white butter dishes, a dozen small test-tubes of short length and not over half an inch in diameter, and a spirit-lamp or Bunsen burner to supply heat. There should also be at hand two small bottles or tubes containing red and blue litmus-paper. The entire outfit is procurable under five dollars.

There are five kinds of artificial silk generally met with in commerce as follows—Collodium silk (strictly nitro-silks), cellulose silks, viscose silks, acetate silks, gelatin silks.

The first important test to make is to determine whether the silk under examination is made from gelatin or not.

Take one of the test-tubes, see that it is clean and dry inside, and place at the bottom of it a small tuft of the silk about the size of a small pea when rolled between the fingers. In the open end of the tube insert a piece of red litmus-paper, bending the end over so that the strip will

not slide down the tube. With a handle made of several folds of paper around the neck of the tube so as to permit one to hold it comfortably, place the closed end of the tube in the flame of the Bunsen burner or spirit-lamp, giving the tube a slight to and fro motion until the fibres in the tube begin to char and vapours are seen to arise. When these vapours are observed to come out of the open end of the test-tube, note whether the colour of the red litmus paper changes to blue. If such a change takes place it is due to the presence of ammonia gas resulting from the charring of the fibres, and which could only come from gelatin silk. These vapours may also have the odour of burning horn or hair, which odour is further indicative of the presence of gelatin.

On the other hand, if the litmus-paper does not change colour, acid fumes may be present, and are to be confirmed by repeating the test, but using *blue* litmus-paper, and upon it turning red indicates that the silk may be any one of the four above named makes. To distinguish finally between the several artificial silks emitting acid fumes with heat place two of the butter dishes side by side; in one, place some of the silk fibre, and upon it pour some of reagent No. 1, and let soak for a few minutes, and then afterwards add a few drops of reagent No. 2. In the second dish put some of the fibre and a small amount of reagent No. 3, and note carefully what changes in colour, if any, take place. If both samples show a distinct yellow coloration, the silk is *acetate silk*.

On the other hand, if the coloration is blue, the silk may be either *collodium*, *cellulose*, or *viscose silk*, which is confirmed if the coloration shown in the second dish is reddish violet. To differentiate between these three silks first mentioned place a small tuft of the fibres in a dry dish, and pour upon it a small amount of cold concentrated sulphuric acid (No. 4). If the silk dissolves rapidly the specimen is either collodium or viscose silk; cellulose silk, *i.e.*, Pauly, Fremery, &c., dissolves slowly.

Confirmatory tests are made in test-tubes with the chromic acid solution (No. 5) in the cold, when these three silks dissolve gradually, and upon the tube being heated dissolve quickly. When treated in the same manner with warm caustic potash solution (No. 6) these three silks, together with the acetate silk, show a distinct swelling, while *gelatin silk* dissolves rapidly and completely.

The copper oxide ammonia test (No. 7) when applied in a test-tube first causes a swelling, and dissolves collodium and viscose silks, but acetate silk swells without dissolving, and gelatin silk takes a bluish violet coloration without dissolving.

The nickel oxide ammonia reagent (No. 8), when applied both cold and warm to a sample of artificial silk in the test-tube, causes a swelling of the fibres but without dissolving them. This applies to collodium, cellulose, viscose, and acetate silk, but not to gelatin silk, which latter takes a brown coloration without dissolving.

The alkaline copper glycerin solution (No. 9) has no action even after long boiling upon the first four silks above mentioned, but gelatin silk dissolves after a short time.

A convenient reagent for artificial silk is the concentrated sulphuric acid diphenylamine solution (No. 10) which has been extolled as the one reagent for this class of work, but as a matter of fact its usefulness is limited exclusively to differentiate only the nitro-silks from the others. With nitro-silks of the Chardonnet type it causes a distinct blue coloration, while the other silks remain uncoloured. This diphenylamine reaction lasts but a comparatively short time, reaching its maximum intensity within five minutes after adding the reagent, when it gradually disappears.

In order to be in the position where one can absolutely and certainly pass judgment upon the identity of a given silk sample, the operator should have at hand a collection of true type samples obtained directly from the artificial silk manufacturers and to make the above outlined reactions repeatedly, systematically, and with care. By care is

meant not being too hasty in forming a conclusion, and to disregard and reject completely any test that one may have made into which the element of doubt enters. With such a set of proved samples at hand and a set of reagents as above outlined, when unusual lots are received by the dye-house, or where silk is received from unfamiliar sources, its identity can be accurately determined.

The foregoing details refer to undyed artificial silk, but to identify dyed silk by chemical means requires that it should be stripped of its colour, which is generally very easily accomplished by means of hydragilite or some other equally efficient stripping agent.—*Chemical Engineer*, xx., No. 5.

## SIR JOHN CASS TECHNICAL INSTITUTE.

### OPENING OF THE METALLURGY LABORATORY.

THE Metallurgy Laboratory for the Mechanical Testing of Metals and Alloys presented to the Sir John Cass Technical Institute by the Worshipful Company of Goldsmiths was formally opened by Sir BOVERTON REDWOOD, Senior Warden of the Goldsmiths' Company, on Wednesday, the 3rd inst., in the unavoidable absence, owing to illness, of Sir Robert Mowbray, Prime Warden of the Company.

The work of this new laboratory, which will form an important extension of the Metallurgy department of the Institute, will be carried on from the Metallurgical rather than from the Engineering standpoint, and will be closely related to the instruction already provided in connection with the Metallographic and Pyrometric examination of metals and alloys, including iron and steel, and the materials used in the motor-car industry and in the construction of aeroplanes, high-speed machinery, and the like.

The equipment which has been provided includes a Buckton's Single Lever Vertical Testing Machine of 30 tons capacity, a Drummond's Centre Screw-Cutting Lathe, an Izod's Impact Testing Machine, a Brinell Hardness Testing Machine, a Sankey Bending Testing Machine, a Shore Scleroscope, together with an electric motor with belts, shafting, &c., for driving the machinery and tools.

Previous to the opening of the Laboratory, Sir Bovertton Redwood distributed the prizes gained by students of the Institute during the past session and delivered an address, the Chair being taken by Sir Thomas Elliott, who has succeeded the late Sir Owen Roberts as Chairman of the Governing Body. In speaking of the work of the Institute Sir Bovertton Redwood said that such work as was being done was never more needed than at the present time. Among other things which the War had done for us, it has shown us that there must be a much more intimate relation between science and industry in this country, and that it was to be hoped that the students would avail themselves to the fullest possible extent of the facilities which the Institute afforded them of becoming better qualified to discharge the duties with which they would be entrusted. If one result of this terrible war is to bring about a better recognition of what is needed in this direction we shall have some compensation for the sacrifices which we are making. We shall, however, always have to reckon with the scientific industrial initiative of Germany, whose competition will certainly grow keener after the war than it has ever been before, and can only hope to hold our own if we diligently apply the lesson which we have learned. There has been far too much disposition among us in the past to complacently adhere to the even tenor of our progress on an empirical basis, whilst Germany has called to her aid all the resources of science, and has shown how successfully science and industry can march together. We must, therefore, set our house in order before the war is over, if we are to take advantage of the opportunity which now lies before us.

In referring to the courses on "Fuel and Power," arranged at the Institute, Sir Bovertton pointed out the

all-important part that is now being played by liquid fuel both in the Navy and on the field of battle on land, especially in connection with the "all-oil boilers" now in use on the battleships of the *Queen Elizabeth* class, all of which are driven solely by oil fuel.

Dealing with the new development of the work of the Metallurgy department Sir Bovertton spoke of the great pleasure it had given the Goldsmiths' Company to be associated with this timely addition to its activities, for they recognised how fully the Mechanical Testing of Metals and Alloys had become of fundamental importance in modern metallurgical practice.

## PROCEEDINGS OF SOCIETIES.

### INSTITUTE OF CHEMISTRY.

#### PROFESSIONAL CHEMISTS AND THE WAR.

AT the thirty-seventh Annual General Meeting of the Institute of Chemistry held at the new premises of the Institute, in Russell Square, on March 1, 1915, Prof. RAPHAEL MELDOLA, the retiring President, congratulated the Fellows and Associates on the approaching completion of their new headquarters, and warmly acknowledged the services of Sir John Burnet, the architect.

Referring to the work of the year, Prof. Meldola indicated the activities of professional chemists in connection with the war. The Council of the Institute had supported the counter manifesto to which many British scholars and public men had subscribed in answer to the document emanating from analogous circles in Germany. The Institute has also been instrumental in directing the attention of the Government to the desirability of appointing a Special Committee to deal with the question of supplies of chemical products for which the country had hitherto been dependent to a preponderating extent upon German factories. Dealing with the question of dye-stuffs, Prof. Meldola reminded the members of the warning he had given in the last paper read before the Chemical Section of the Society of Arts in 1886. Systematic enquiries made among the consumers revealed the fact that even at that time 90 per cent of the dye-stuffs then in use here were of foreign manufacture. No lost ground has been regained, and before the outbreak of the war we were still importing nine-tenths of our colouring matters from Germany and Switzerland. The development of this industry abroad had been due to the recognition and utilisation by manufacturers of the results of chemical research. Early in August the President of the Board of Trade appointed a Committee, under the chairmanship of Lord Haldane, for the purpose of advising the Government with respect to the means of meeting the national requirements, and from this Committee there was subsequently formed a Sub-Committee under the chairmanship of Lord Moulton, for dealing especially with the manufacture of dye-stuffs. A scheme formulated by the Government in consultation with a Committee representative of the great dye-using organisations was put forward early this year, and after full discussion by those immediately concerned was finally referred back for modification. The scheme was considered unsatisfactory, but the Government determined not to allow the project to fall through, and a new scheme, which differed from the first in certain important particulars, was subsequently launched. A considerable number of the dye-consuming companies appeared to be favourably disposed towards it. It should be clearly understood, however, that neither the Board of Trade Advisory Committee nor the Dye-stuffs Sub-Committee was in any way responsible for either of these schemes. The grounds on which public action was imperatively called for were set forth most clearly in an Address delivered by Lord Moulton at Manchester, on December 8, 1914. He had stated explicitly that he only held himself

responsible for the advice that the Government should take action, but not for the particular shape or form which that action should assume.

The principle had been adopted that there should be established a company, in which the consumers should be the chief shareholders, and which the Government should subsidise by advancing capital at a certain rate of interest to the extent of £1,000,000. The scheme was in a way a co-operative one, and for the first time in this country a distinct proposal was made for the establishment of a State-aided industry. In view of the great interests at stake the policy appeared to be a sound one, and this was admitted by both political parties when the proposal was mentioned in the House of Commons in November by the President of the Board of Trade. It was a matter of importance to the representatives of the chemical profession that their aspect of this great industry should be kept well to the fore in the scheme, and in any other scheme that might hereafter be put forward. They desired to see the restoration of the coal-tar colour industry to this country, and not only restored but permanently retained after the war. The discussions of the Government schemes in various parts of the country by dye-consuming organisations, chambers of commerce, and so forth, had all centred round political or economic questions; the vital principles, viz., adequate chemical control, had been subordinated or left out of consideration altogether. While there was much wrangling over the question as to the method by which the industry should be established and maintained here, whether by free trade or protection, or subvention, or by any other device, the consideration of the questions whether a few years hence there would be anything in the way of dye-stuffs worth protecting, and whether there would be a sufficient basis of material products left for the politicians and economists and business people to wrangle over was overlooked. It was not a purely business problem which the Government had undertaken to solve; it was primarily a chemical problem. It was not even a business problem in the ordinary trade sense, because the main object was at first to supply our own wants, and the chief consumers were to be the chief producers. The question of business in the sense of export trade was, for the present, remote.

The conditions which had to be met if this country was to be once more the home of the colour industry were certainly imperfectly understood by the public. Even those most concerned—those who were invited to subscribe to the capital—appeared in most cases to have an idea that all that was necessary was to find the money, secure the Government aid, appoint a Board of business Directors, and lo! the industry would forthwith spring into existence ready to cope with all emergencies. What were the facts of the case? About five hundred different dye-stuffs of definite composition had been given to tinctorial industry as the products of chemical research. Of these a certain number only could be and were being made in this country. The total output of our factories was at present inadequate for the requirements of our textile industries. The first steps to be taken therefore were to enlarge and develop existing factories so that the dyes which could be made here should be turned out in larger quantities. This necessity has been provided for in the Government scheme, and "so far so good." If the extension of the existing factories still produced insufficient supplies, new factories must be erected and equipped. This also was provided for in the scheme; but if we want to establish the industry here permanently we must look beyond all this. Where should we be left after the war? We should be in possession of processes for making a certain number of dyes, and the supply of their products might possibly be sufficient for the particular purposes for which they were required; but there would still be an outstanding number of other products which had never yet been made here, and for the working out of these processes no combination of "business" talent was of the slightest value. It was not a business question but a chemical question, and it was by chemical research alone

that our colour industry would be saved. The German colour industry has been built up by the utilisation of the results of research carried on in the factories and universities and technical schools for a period of over forty years! To suppose that we could retrieve our position by starting a company, the directorate of which was to consist solely of business people, was ludicrous. The large and representative body of dye users and producers which form the Dye-ware Supply Enquiry Committee of the Society of Dyers and Colourists fully endorsed this view, and forwarded to the Board of Trade a resolution, passed at Manchester last month, in support thereof. It was satisfactory to learn that there were dye-consuming organisations which had grasped the situation scientifically. To imagine that a dyer, however skilful he might be, was, by virtue of his occupation, necessarily competent to direct the affairs of a company concerned with the manufacture of the dyes which he used was about as sensible as the assumption that a person who could tell the time by his watch was thereby qualified to undertake the direction of a factory for the construction of chronometers.

One feature of the new scheme which the chemical profession would view with favour was the distinct recognition of research as a necessity for the development of the industry. The Government "will, for ten years, grant not more than £100,000 for experimental and laboratory work." That was certainly a concession which marked an advance in official opinion for which they were grateful. It would be for the satirist of the future to point out that it required a European war of unparalleled magnitude to bring about this official recognition of the bearing of science upon industry! Who was to direct this research? A directorate of purely business people would certainly be incompetent; a Board composed of dye users could do no more than indicate what dye-stuffs were needed. True, it was proposed that the company should take powers to secure the assistance of a committee of experts, but this appeared to be simply a reversion to the policy of "drift." The experts were, as usual in this country, to be subordinated, and their assistance was to be invoked at the discretion of a Board, the members of which could have no real knowledge of the conditions necessary for producing the materials they required. Would they be competent to point out dangers ahead? The "staple products" upon which they were asked to stake their capital might a few years hence be superseded by the products of subsequent discovery. The policy of attempting to run a highly specialised and rapidly developing branch of organic chemical industry by a company of business people with expert assistance when required was fatal if it was intended to establish the industry permanently here. The group of industries which had arisen from the products of the tar still was not going to remain stagnant after the war, and it was scientific guidance and not mere assistance that would keep them alive. It was the expert, and the expert only, who could foresee the course of development, who could keep in touch with the progress of research, and direct with intelligence the campaign against competitors. If such scientific direction was withheld all schemes were sooner or later bound to end in failure. If this second warning to the country after a period of about thirty years were unheeded it would be so much the worse for the country!

To other branches of manufacture in which our dependence upon foreign products had been forcibly revealed by the war, professional chemists were able to render considerable service. It had long been known that laboratory glass and porcelain apparatus and filter-paper had been mainly supplied from abroad, and that large quantities of pure chemical reagents and of the special chemicals required for analytical or research work had borne non-British labels. This state of affairs called for prompt action, and the Councils of the Institute of Chemistry and the Society of Public Analysts had acted conjointly as a Committee for dealing with this matter of such vital importance to the profession. The inquiries instituted by

this Committee soon brought the fact that failure in the supply of laboratory glass apparatus would not only cripple the work of the chemists, but would also influence to a serious extent certain important industries the dependence of which upon supplies of suitable glass had not at first been foreseen. In connection with these inquiries, it was at a later period considered necessary, in view of the great national interests involved, that the Institute should take part in giving practical aid to would be manufacturers. For this purpose a Glass Research Committee was appointed, and was still carrying on its work. Formulas supplied by members of the Committee had been made in the laboratory of the Institute and submitted to the recognised tests. The experiments had perforce been carried out on a small scale, but the co-operation of a number of glass manufacturers had been secured, and the results would be tested on a fairly large scale under complete expert control. Not the least important of the glass problems was the production of a suitable glass for miners' safety lamps, the necessary protecting shades for which had also been hitherto mainly imported from abroad. This particular kind of glass was of pressing importance in relation to coal-mining, and it was certainly humiliating to learn from the makers of these lamps that for glass of the required quality capable of complying with the Home Office tests, we have been so largely dependent upon foreign glass manufacturers. The action of the Institute throughout had been governed entirely by patriotic motives; the work was being carried on as a national duty, and the results were placed unreservedly at the disposal of all manufacturers who wished to avail themselves of them. The efforts made by certain firms, as well as by our own Committee, were leading to results which held out a good prospect of the manufacture of many kinds of chemical glassware being established on a permanent footing in this country, so that at no distant future British laboratories would be stocked with home-made apparatus. With respect to porcelain, it was satisfactory to be enabled to report that crucibles and dishes equal to the best Berlin ware were now being produced in this country at practically the same price. It was equally gratifying to know that the filter-paper problem had also been practically solved—thanks largely to the assistance given by our paper experts—and that British filter-papers of all the required qualities, and in every respect equal to those which had been associated with foreign labels, would surely be manufactured in British mills.

With respect to the supplies of chemical reagents, the Joint Committee found it necessary to entrust to a special Sub-Committee the somewhat arduous task of compiling a list of all the commonly used reagents with indications of the standards of purity required and the tests necessary for ascertaining whether the required standard had been reached. The list had been published as a pamphlet, and had been sent to many firms and companies of manufacturing chemists with a view to ascertaining which reagents of their own manufacture they were prepared to supply. When the replies had been received the Joint Committee would know the requirements of the profession could be met by British manufacturers.

In all the branches of their work the Joint Committee had received most cordial assistance from manufacturers and dealers. The manufacturers of chemical reagents were doing their best to meet the needs of the profession. It was most earnestly hoped that sooner or later laboratory supplies both of apparatus and materials would be entirely of British origin. The manufacturers were in some cases, at considerable cost developing lines of industry which were of the nature of new departures for this country. It was the solemn duty of consumers and users—in fact of every branch of the profession—to do their utmost to encourage and support these new home industries. Patriotism and the credit of our country alike demanded that, after the war, they should help those who were helping them now, by insisting upon having nothing but the products of British manufacture. They should not only assist in the

development of these industries now, but insure their permanent retention after the declaration of peace. With the achievement of this result there would be removed the reproach that the nation which gave to chemical science Priestley, Black, Boyle, Cavendish, Davy, Dalton, Faraday, and Graham—the country which founded the coal-tar colour industry, and which had taken the lead in the manufacture of "heavy chemicals," allowed her laboratory work to be dependent upon foreign materials, and her great textile and metallurgical industries to be threatened through the stoppage of supplies from inimical countries.

Continuing, Professor Meldola referred to the large number of Fellows, Associates, and Students who had for the time being relinquished their professional work or their studies in order to give their services to the country in the field of war. It was of interest to learn that during the present campaign a mobile chemical laboratory has been in use at the front. Professional chemists were also serving with the Army Service Corps and with the Sanitation Companies of the Royal Army Medical Corps. Members also were engaged in laboratories and factories under Government control and concerned with the testing or production of the various war materials and supplies. The Institute, in brief, had done its best in the present emergency to discharge its functions as a national professional organisation.

The Government departments early in August received intimation that the services of technical experts and the accommodation of the Institute's laboratories were at the disposal of the Government if needed, and the names of many members were included in Government and other Committees carrying on work of supreme importance to the welfare of the country at the present time. While he recognised that, under the existing conditions of strain upon all State officials, individual interests had to give way to national requirements, he felt that the Government Departments did not hold that official view of the status of the chemists which they should. He referred to the advertisement recently issued by the Chief Inspector at the Royal Arsenal, Woolwich, inviting applications from temporary assistant chemists, the candidates being expected to have a thorough training in inorganic and organic chemistry, to be accurate analysts, preference being given to University graduates or to Members of the Institute. The remuneration offered for the positions was expressed as "wages £2 os. 6d. per week." A more direct discouragement to entry into the profession of chemistry, or a more certain method of securing incompetence for the service, could scarcely be imagined. It was particularly unfortunate that such degrading terms should be offered at a time when the nation's need for skilled chemists was being made manifest from so many different quarters, and when this necessity was just beginning to be realised.

#### ROYAL SOCIETY.

*Ordinary Meeting, February 25, 1915.*

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Effect of the Depth of Pulmonary Ventilation on the Oxygen in the Venous Blood of Man.*" By Prof. L. HILL, F.R.S., and J. F. TWORT.

"*Effect of Functional Activity upon the Metabolism, Blood Flow, and Exudation in Organs.*" By J. BARCROFT, F.R.S., and TOYOJIRO KATO.

The organ studies have been skeletal muscle and the submaxillary gland.

1. The oxygen used by these organs not only increases during their activity but outlasts it by some hours. The curve of oxidation usually shows two maxima, the first during the period of activity, the second much later.

2. Water leaves the blood vessels in much greater quantities during and after activity of the organs than before, a similar second maximum is sometimes seen in the case of the exudation.

3. In the case of muscle not all the exudation leaves the muscles as lymph. Of the right and left gastrocnemius muscles, the one which has been stimulated is heavier several hours after the stimulation, and of lower specific gravity than the unstimulated one.

4. The dilatation of the vessels of the organ outlasts the functional activity for two hours or more in the case of muscle which has been stimulated rhythmically for 15 minutes.

5. The tenseness of the muscle caused by its distension with water would seem to be the physical basis of stiffness.

"Osmotic Balance of Skeletal Muscle" By Miss D. JORDAN LLOYD.

In order to free the phenomena as far as possible from complications due to the formation of diffusion columns, a very small flat muscle—the sterno cutaneous of the frog—was used. In solutions of non electrolytes of from zero to about 0.25 mol concentration, and in solutions of electrolytes of from zero to about 0.14 mol, this muscle at first increases in weight and then decreases, finally falling considerably below its initial weight. The amount of increase and of decrease and the time relations are determined by the previous history of the muscle, the chemical constitution of the solute, and the concentration of the solution. This communication will be confined to the first of these variables.

Previous treatment with oxygen by suspending the muscle in the gas saturated with aqueous vapour reduces and finally obliterates the initial rise in weight. After exposure for six hours to oxygen a muscle slowly loses weight even in distilled water. After exposure to hydrogen for three hours the muscle in distilled water increases 85 per cent in weight. Sixteen hours' exposure to air still leaves a slight initial rise.

The muscles in moist oxygen either gained slightly in weight or lost weight. In moist air the muscle lost weight. In moist hydrogen there is a slight gain in weight.

These results show that an oxygen-saturated muscle has an osmotic equivalent less than that of distilled water. The initial absorption of fluid may be regarded as due to unavoidable stimulation of the muscle during its removal from the animal. Removal occupies five minutes. During it some absorption will probably occur.

The difficulty of freeing distilled water from toxic substances is well known. This difficulty is done away with by exposing the muscle only to water vapour of a known pressure. A muscle saturated with oxygen loses weight in water vapour saturated with respect to a plane surface of distilled water. The vapour pressure of the muscle is therefore greater than that of water. The vapour pressure of a muscle not saturated with oxygen, that is to say, which is in air, is at first less than that of distilled water. A remarkable feature of this muscle is the wide change in water content needed to make a small change in vapour pressure. A muscle behaves quite differently in the vapour of 0.13 mol. Ringer to what it does in the vapour of 0.125 mol. Ringer.

"Function of Chlorophyll" By A. J. EWART, D Sc.

Previous observations of the author have tended to support the theory that chlorophyll is a stage in photosynthesis. The present paper develops this idea further.

By means of Wellstatter's methods of extraction and separation, chlorophyll, carotin, and xanthophyll were obtained in the pure state and used for the experiments. The following conclusions were reached—

1. No peroxides, organic or inorganic, are produced during the photooxidation of chlorophyll, xanthophyll, and carotin. The oxidising effect of these latter substances on potassium iodide when they are undergoing

oxidation in the light is due to the fact that in the presence of abundant oxygen they can act as oxydases, not only to themselves, but also to substances with which they may be in contact, such as hydriodic acid, litmus, or guaiacum.

2. Chlorophyll and xanthophyll and xanthophyll decompose during photo-oxidation into (a) solids and (b) a gas. The solids are colourless waxy substances and hexose sugars. The gas is formaldehyde gas. With dry films in dry air free from CO<sub>2</sub> relatively more formaldehyde is produced and less sugar.

3. Carbon dioxide combines with chlorophyll forming xanthophyll and a colourless waxy solid. The combination only takes place actively in the presence of water, and is accelerated by sunlight.

It is suggested that in this last reaction a portion of the oxygen liberated may oxidise the xanthophyll in presence of sunlight to formaldehyde, sugar, and phytol, the latter retaking its place in the tricarboxylic chlorophyll grouping. There is some evidence that possibly chlorophyll may be built up from xanthophyll and the products of the photo oxidation of chlorophyll. In any case it seems clear that the assimilation of carbon dioxide involves a complex series of reversible chemical changes in which chlorophyll and xanthophyll play a direct chemical part, and in which light acts as an accelerating and possibly as a directive agency.

"Influence of the Hydrogen Ion Concentration upon the Optimum Temperature of a Ferment." By A. COMPTON.

"Functional Edema in Frogs." By M. BACA, K. M. COGAN, and A. E. TOWERS.

## NOTICES OF BOOKS.

*Air, Water, and Food from a Sanitary Standpoint* By ALPHEUS G. WOODMAN and JOHN F. NORTON. Fourth Edition. New York John Wiley and Sons, Inc. London Chapman and Hall, Ltd. 1914.

THE text of this book has been carefully revised, special attention being paid to modern views on the relation of air to health and comfort. The main object of the work is to arouse interest in chemical sanitation and to educate public opinion upon the subject. The book has moreover a value as a text book for the use of students in technical colleges and schools, and the discussions concerning the principles involved in analytical methods and the correct interpretation of results are full of useful information for general purposes. The actual processes of analysis and the detection of common adulterants are also described, and a first course of work on food analysis could well be based upon the text.

*Tables Annuelles de Constantes et Données Numériques, de Chimie, de Physique, et de Technologie.* ("Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological") Paris Gauthier-Villars Leipzig Akademische Verlagsgesellschaft. London J. and A. Churchill. Chicago University of Chicago Press. 1914.

THE third volume of this important work is now published. The further advances in our knowledge of constants have been included, and the general plan of the work remains unaltered. The subjects of electrons, ionisation, X-rays, and radio activity have naturally been greatly extended. Published as it is under the direction of an International Committee with Dr. Ch. Marie as general secretary, the value is unquestionable, and we hope that the great labour of keeping the work up to date will not be hindered by the present European upheaval.

We notice from the errata pages given at the end of the work that there has been a steady improvement in the successive volumes, and in the present issue they are both few and unimportant.



## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cx., No. 5, February 1, 1915.

**Phototropism of Inorganic Systems.**—José R. J. de Mourcelo. —To prepare phototropic systems with strontium sulphide the author precipitated pure strontium carbonate from the nitrate by means of sodium carbonate. He then added anhydrous sodium carbonate and sodium chloride, incorporated the active material with the mixture, and finally added flowers of sulphur. The crucible containing the mixture was then raised to a red heat for four hours. The phosphorogens used were manganese and bismuth. It was found that manganese alone is a phototrope as well as a phosphorogen, but it was not possible to establish any relation between the intensity of the phosphorescence and the phototropism. Nor did there appear to be any relation between the proportion of active substance dissolved in the strontium sulphide and the sensitiveness of the system to direct light. When both manganese and bismuth were used it was found that the phototropism of the system was more constant.

## MISCELLANEOUS.

**Literary Intelligence.**—Timely in its appearance is the new book on "Explosives," by Mr. A. Marshall, A.C.G.I., F.I.C., F.C.S., Chemical Inspector, Indian Ordnance Department, which is to be ready this month. This new treatise, which is fully illustrated, deals exhaustively with the Manufacture, Properties, Tests, and History of Explosives. Messrs. J. and A. Churchill are the publishers.

**Royal Institution.**—A General Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton Browne, Treasurer and Vice-President, in the Chair. Prof. E. G. Coker, Mrs. de Laszlo, Dr. A. L. Armitage Forbes, Mr. Charles J. Singleton, and Mr. F. Coston Taylor were elected Members. The following letter, addressed by the Hon. Sir Charles A. Parsons, K.C.B., F.R.S., to Sir James Crichton Browne, Treasurer of the Royal Institution, was read:—

"14 February, 1915.

"DEAR SIR JAMES,—It gives me much pleasure to enclose cheque £5000 in favour of the Royal Institution, which may be of some help at the present time.—Yours very sincerely, CHARLES A. PARSONS."

The following Resolution passed by the Managers was approved by the Members:—Resolved, that the Managers of the Royal Institution desire to express to the Hon. Sir Charles A. Parsons, K.C.B., F.R.S., who has unconditionally placed at their disposal, for the purposes of the Institution, the sum of £5000, their most grateful appreciation of his munificence and discernment. They accept the Gift as a timely and noble recognition of the good public work the Institution has done in the past, and is still doing, in the acquisition and diffusion of Scientific Knowledge, and as an incitement to maintain and extend its usefulness in the unique position which it has for more than a century occupied.

**American Chemical Society.**—The American Chemical Society is one of the largest organisations of scientists in the world, having now over 7100 members, including nearly all the prominent chemists in America, and many foreign chemists as well.

**New Orleans Meeting.**—The Fiftieth Meeting of the American Chemical Society will be held in New Orleans

from Wednesday, March 31, to Saturday, April 3, inclusive. The opening meeting and the Symposium of the Industrial Division will be held at the Tulane University of Louisiana. The meetings of divisions will be held in the Grunewald Hotel. There will be an excursion to the Salt Mines at Avery's Island, Saturday, April 3. The mines themselves are well worthy of a visit, being of peculiar geological formation and interesting historically. The immense chambers hollowed out in the salt some five hundred feet under ground and the unusual pure quality of the salt itself have rendered these mines famous. The trip to Avery's Island, which is approximately 130 miles from New Orleans, carries one into the Teche country, made famous in the story of Evangeline, and through now fertile lands only recently reclaimed from the marsh by means of scientific irrigation. The mines are being worked five hundred feet below the surface and the supply of salt is practically inexhaustible. A feature of the meeting will be a symposium by the Industrial Division, which was originally planned for the Montreal meeting. Some thirty papers have been promised, giving resumé of the progress of American chemistry during the time covered by the fifty meetings held by our Society. The whole of Thursday, April 1, is to be given up to this symposium. It is to be opened by an address by A. D. Little presenting broadly and adequately some of the vast opportunities open to the South in the Chemical Industry.

**Seattle Meeting.**—The summer meeting of 1915 will be held in Seattle, August 31 to September 3, inclusive. Following the Seattle Meeting a day will be spent in Portland, Ore., and the members will then continue together to San Francisco for a social session of one evening there.

## NOTES AND QUERIES.

\* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Cellulose Acetate.**—A correspondent asks for the addresses of any British manufacturers or dealers in cellulose acetate.

## MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Royal Society of Arts, 8. (Cantor Lecture). "House Building," by M. H. Baillie Scott
- TUESDAY, 16th.—Royal Institution, 3. "The Belief in Immortality among the Polynesians," by Prof. Sir J. G. Fraser.
- WEDNESDAY, 17th.—Royal Society of Arts, 8. "The Industrial Uses of Coal-gas," by H. M. Thornton.
- Microscopical, 8. "New Mitotic Structure Disclosed as the Result of New Technique," by E. J. Sheppard. "Notes on the Structure of Tests of Fresh-water Rhizopoda," by G. H. Wailes.
- THURSDAY, 18th.—Royal Institution, 3. "The Form and Structure of the London Basin" by Dr. Aubrey Strahan.
- Royal Society. "X-rays and Crystals," by Prof. Bragg. (The Bakerian Lecture).
- Royal Society of Arts, 4.30. "The Indian Army," by Lieut.-Col. A. C. Yate, I.A. (retired).
- Chemical, 8.30. "Relation between Viscosity and Chemical Constitution—Part IX., Viscosity and Fluidity of the Aliphatic Acids," by A. E. Dunstan. "Methylated Derivatives of a New Form of Glucose," by J. C. Irvine, A. W. Fyfe, and T. P. Hogg. "Velocity of Crystallisation from Aqueous Solutions," by N. P. Campbell. "Studies in Phototropy and Thermotropy—Part VII., Polymorphic Vanillidenearylamines produced by Trituration and by the Influence of Actinic Light," by A. Sender and R. B. Forster. "Organic Derivatives of Silicon—Part XXIII., Further Experiments on the so-called Siliconic Acids," by J. A. Meads and F. S. Kipping.
- FRIDAY, 19th.—Royal Institution, 9. "The Modern Piano Player—Scientific Aspects" by Prof. G. H. Bryan.
- SATURDAY, 20th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

# THE CHEMICAL NEWS

VOL. CXI., No. 2886.

## NOTES ON GLASS.\*

THE enclosed notes explain themselves; they summarise some recent work on glass vessels:—

A certain amount of experimental work on glass-ware of various kinds has been carried out recently at the National Physical Laboratory, and it may be of interest to make known some of the results.

Chemical investigations have for some years been dependent on German glass; the publication of the analyses and of test results may, it is hoped, lead some English firms to produce articles which may replace those of German manufacture.

The first table gives the analyses of some Thermometric and Chemical glass-ware.

### Resistance of Various Chemical Glassware to the Action of Chemical Attack.

The table below, taken from the work of Mylius and Forester on this subject, gives the action of various chemical reagents on glass used for chemical purposes (for analyses, see Table A).

Type of glass.	Water.		H <sub>2</sub> SO <sub>4</sub> .	NaOH.	Na <sub>2</sub> CO <sub>3</sub> .
	20°.				
	20°.	80°.			
"R" ..	0'0054	0'0144	0	41	23
Jena ..	0'0071	0'0035	0	53	19
Bohemian ..	0'118	0'219	5	37	49

Type of glass.	Flasks.		H <sub>2</sub> SO <sub>4</sub> .	NaOH.	Na <sub>2</sub> CO <sub>3</sub> .
	Water.				
	20°.	80°.			
"R" .. ..	0'0128	0'0128	0	51	26
Jena .. ..	0'0063	0'0057	0	63	24
Bohemian ..	0'0093	0'255	11	52	70

The figures are in mgrms. per sq. dcm.

The solutions, viz., 2N NaOH and N H<sub>2</sub>SO<sub>4</sub> were allowed to act at 100° for six hours, and 2N Na<sub>2</sub>CO<sub>3</sub> for three hours.

The Jena glass used was probably of the composition given on Table A under description "Original." This glass is now not used, but has been replaced by the new Jena glass, an analysis of which has been made at the N.P.L. Soon after the introduction of this new Jena glass by Schott and Gen., viz., in 1910, some tests were made at the N.P.L. A special feature of the new glass was its increased resistance to attack; this was brought about by long exposure to sulphurous gases. The tests on the glass before and after such treatment is given in the table. Several kinds of vessels were tested, and the results for all were substantially the same.

There was a small improvement as regards resistance to the attack of water, but no improvement to the attack of alkalis. Since its introduction this type of glassware has been used in the N.P.L. and has given every satisfaction.

It is well known that alkaline fluids attack glass very markedly, and for that reason in chemical analyses prolonged contact is avoided. To do this is not always possible, e.g., in the estimation of zinc and manganese especially in silicate analyses. It is necessary in the estimation of these metals to employ solutions containing alkaline chlorides and ammonium sulphide and to allow the solutions to stand at a rather higher temperature (50–60° C.) for some times as long as twelve hours. In these circumstances the glass is invariably attacked, and

\* From the National Physical Laboratory.

### Tests on "New" Jena Glass made at the N.P.L. in 1910.

1. Vessels had received no annealing.
2. Vessels had received ordinary annealing.
3. Vessels had received special annealing in sulphurous gases for thirty-six hours.

Mgrms. Na<sub>2</sub>O per sq. dcm. given up to water at 20° C. in one week.      Mgrms. Na<sub>2</sub>O per sq. dcm. given up to water at 80° C. in three hours.

#### Beakers—

1.	0'0022	0'0045
2.	0'0032	0'0047
3.	0'0019	0'0040

#### Loss in Weight in Mgrms. per sq. dcm.

3 hours with 2N NaOH at 100° C.      3 hours with 2N Na<sub>2</sub>CO<sub>3</sub> at 100° C.      6 hours with N H<sub>2</sub>SO<sub>4</sub> at 100° C.

#### Beakers—

1.	51	9	Nil.
2.	51	8	Nil.
3.	55	7	Nil.

#### Conical flasks—

1.	63	8	Nil.
2.	60	11	Nil.
3.	71	10	Nil.

#### Flat-bottomed flasks—

1.	62	8	Nil.
2.	71	8	Nil.
3.	79	6	Nil.

although no quantitative experiments have been made with the Jena glass, the resistance to the attack of these solutions is certainly not as good as with the alkaline solutions in the absence of chlorides and sulphides. In view of the fact that glass flasks have to be used for this purpose, it seems desirable to devise a test, in addition to the tests usually carried out, to determine the ability to withstand the joint action of alkaline chlorides and sulphides.

The New Jena Glass examined at the N.P.L. in 1910 possessed in a very high degree the ability to withstand sudden change of temperature. A glass flask filled with molten paraffin wax at a temperature of 250° C. broke when placed suddenly in water at 15° C., but only after successfully standing such a test at slightly lower temperatures.

Another question which is engaging attention is glass for miners' lamps, incandescent chimneys, steam gauge tubes, and other purposes in which a gradient of temperature is established between the inside and outside.

Analyses of some of these are given in the following table:—

#### Analyses of Lamp Glasses.

	I.	II.	III.	IV.	V.
Silica ..	73'88	74'28	51'26	54'92	76'78
Alumina ..	2'24	3'24	6'90	1'28	0'72
Lime ..	trace	trace	trace	trace	6'52
Zinc oxide ..	trace	trace	7'16	0'82	—
Manganese oxide ..	trace	trace	trace	trace	trace
Ferric oxide ..	trace	trace	trace	trace	trace
Lead oxide ..	—	—	27'54	34'93	—
Soda (Na <sub>2</sub> O) ..	6'67	6'73	trace	2'08	11'14
Potash (K <sub>2</sub> O) ..	trace	trace	2'67	4'54	4'74
Boric anhydride ..	16'48	15'02	3'97	—	—
Magnesia ..	trace	trace	trace	0'20	0'24
Arsenious oxide ..	0'73	0'73	—	0'99	—
Antimony oxide ..	—	—	0'50	—	—

100'00 100'00 100'00 99'76 100'14

I. Jena Incandescent gas (Schott and Gen.), best quality.

II. Miners' lamp glass (German make), Mark A [I] Bx.

III. Miners' French lamp glass (yellow).

IV. Miners' French lamp glass (colourless).

V. Austrian lamp glass, "Sun Brand."

TABLE A.—Analyses of Thermometer and Chemical Glassware.

	Thermometer glasses.		Schott and Gen., Jena.		Chemical glassware.		
	Jena 59".	Jena 16".	Original.	"New."	Resistance "R."	Kavaller's Bohemian.	Thuringen.
Silica .. .. .	72.86	66.58	66.74	64.60	68.00	76.02	74.36
Alumina.. .. .	6.24	3.84	2.77	6.24	2.32	0.64	0.90
Lime .. .. .	0.35	7.18	0.28	Trace	4.80	7.38	9.40
Zinc oxide .. .. .	—	6.24	8.28	10.43	2.40	—	—
Manganese oxide .. .	Trace	0.28	0.65	Trace	0.14	Trace	Trace
Ferric oxide .. .. .	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Lead oxide .. .. .	—	—	—	—	—	—	—
Soda, Na <sub>2</sub> O .. .. .	9.82	14.80	8.99	9.71	10.17	7.60	14.83
Potash, K <sub>2</sub> O .. .. .	0.10	Trace	0.08	Trace	1.82	7.70	0.14
Boric anhydride .. .	10.43	0.91	7.18	8.70	5.53	—	—
Magnesia .. .. .	0.20	0.17	4.50	0.32	5.04	0.30	0.16
Arsenious oxide .. .	—	—	—	—	0.24	—	—
	100.00	100.00	99.47	100.00	100.46	99.64	99.79

Analyses marked with an asterisk have been made at the National Physical Laboratory. The other analyses are taken from a paper by Walker in the *Journ. Am. Chem. Soc.*, 1905, xxvii., 865.  
Bohemian and Thuringen glass is now rarely used in chemical work, but the analyses given are of the best material of that class.

It appeared, however, from Hovestadt's book on Glass, and other information, that the additional strength of the German glass was conferred on it in great measure by its heat treatment, and tests were made to investigate the state of strain in the glass.

For this purpose the following glasses were examined:—

1. A miners' lamp chimney of white glass of German manufacture.
2. A miners' lamp chimney of yellow glass of French manufacture.
3. A piece of "Durax" tubing as used for chemical purposes.

From each of these tubes two rings of about 1 cm. depth were prepared by making transverse cuts across the tubes; the plane surfaces of the rings were optically polished. One ring of each specimen had a piece cut out so that the ring was free to spring. Other pieces were prepared for the determination of the refractive properties of the glasses.

The three open and three complete rings were examined in plane polarised light for strain. The examination showed that in both rings of the French glass, and in the open ring from the German lamp chimney, the amount of strain was negligible. In the unbroken ring from the German chimney there was very decided strain. Strain was also present in both rings of the Durax glass, the unbroken ring of this material showing much more pronounced strain than any of the other rings. The appearance presented by the rings when examined in the dark field is a very strong and sharp black circular line in the middle of the glass with a decided black cross upon it and the rest of the ring either white or milky.

The character of the strain present in the unbroken ring from the German chimney was determined by distorting the ring into an elliptical form by compression between two points at opposite ends of a diameter of the ring inclined at 45° to the plane of polarisation. By this means the milkiness could be made to disappear entirely from the regions about the diametral plane perpendicular to the line of compression, but the strain in the neighbourhood of the points of compression was increased. This shows that the strain is relieved by an increase in the curvature and augmented by a reduction in the curvature; in other words, the inner layers of the ring are in a state of tension and the outer layers in a state of compression. The fact that in the open ring the strain throughout is practically entirely relieved suggests that these chimneys are made in one operation, and not by the combination of layers of material at different temperatures. It is evident that with

the distribution of strain in the cold state indicated above, the chimney will tend to be relieved of strain when there is a radial temperature gradient throughout its substance with the outer surface cooler than the inner surface.

With the Durax tubing there is in neither ring freedom from strain. In the open ring the strain becomes worse on altering the curvature in either direction. Perhaps this indicates that the tube is built up of layers of the same or different materials, but brought together with one layer decidedly cooler than another. The presence of a thin white band in the substance of the glass may also indicate that the tube has been built up in the way suggested. An examination of all the rings in ordinary light showed the presence of striae likely to prevent the formation of really sharp spectrum lines in the determination of their refractive properties. This expectation was fully borne out by the appearance of the lines in the refractometer. No indication was obtained that any tube consisted of more than one type of glass, but the want of sharpness in the lines was sufficient to obscure the difference between glasses of very nearly identical optical properties. The results obtained in these measurements are as follows:—

	$n_D$	$n_C - n_r$	$v$
German chimney .. ..	1.4795	0.00729	65.8
French chimney .. ..	1.5748	0.01313	43.8
Durax combustion tubing ..	1.5156	—	—

The optical glasses which resemble the above in refractive properties are, for the German chimney one of the new "Fluor Crowns," for the French chimney a light flint, and for the Durax tubing a hard crown.

Experiments were made to determine possible variations in the strained condition of lamp chimneys due to internal heating and resulting temperature gradient across the glass.

Coils of wire were wound round a cylindrical metal core, the whole enclosed in asbestos paper and fitted closely (without mechanical strain) into the ring of the chimney examined. A thermo-couple was introduced between the lagging and the glass to enable the temperature of the latter to be determined on the passage of a current through the heating coil.

*French Chimney.*—This was initially when cool without strain. On heating up strain was found to develop progressively as the temperature rose, and there is no evidence that at any temperature the strain declines to a minimum again.

*German Chimney.*—When cool and at uniform temperature this showed very decided strain in the shape of a

central ring and cross. On heating up the ring the strain was relieved, but the glass is never entirely freed from the strain, as evidenced by a complete absence of the stauroscopic figure. The tendency is rather for the central dark ring to move outwards, and to be replaced eventually by another ring moving out from the inner surface of the glass ring. There is nevertheless a decided minimum effect, i.e., minimum strain, obtained when the temperature of the inner surface of the glass ring is about  $150^{\circ}\text{C}$ . ( $\pm 20^{\circ}$ ). The temperature gradient across the glass is such that in the steady state the temperature of the outer surface of the lamp, corresponding to the above internal temperature, is roughly  $70^{\circ}$ , within the same limits of accuracy. Excessive heating above these limits results merely in producing a more pronounced strain.

A further chemical analysis confirmed the view that the German miners' lamp chimney is of a single material.

The incandescent lamp chimneys are very thin, and optical examination is not possible, but it appears fairly certain that in their case also the extra strength is attained by some process whereby the outside is chilled before the interior cools down. It seems possible also that the extra heat-resisting qualities of certain beakers, flasks, &c., of German glass may be due to the converse process, the interior being chilled previously to the exterior. All these glasses appear to be of the borosilicate type, such as is used for the well-known thermometer glass 59", but with somewhat more boric anhydride; the chemical glass contains zinc oxide, which is absent from the thermometer glass.

As already stated, the object of these notes is to put such information as is available before English manufacturers in the hopes of encouraging some of them to take up the manufacture of some of these glasses.

February, 1915.

## THE PREPARATION OF THE CHLORIDES OF SILICON.

By F. STANLEY KIPPING.

IN a paper published in a recent volume of the *Transactions of the Chemical Society* (1914, cv., 2836) Martin first refers to Oersted's method for the preparation of silicon tetrachloride, and then to the process devised by Gattermann and Weinlig, by means of which silicon tetrachloride, disilicon hexachloride, and trisilicon octachloride may be obtained from crude heated silicon. He then continues:—"Up to the present time this has proved by far the easiest method of preparing not only silicon tetrachloride but also disilicon hexachloride and the higher chlorides of silicon." "After much preliminary work it was found that commercial 50 per cent ferrosilicon, such as is used for refining steel, can be used instead of the expensive silicon itself for the purpose of preparing disilicon hexachloride in quantity, and that this material forms by far the most economical method of preparing silicon tetrachloride. In fact, there can be no doubt that in the future 50 per cent ferrosilicon must prove the starting-point for the preparation of all the chlorinated compounds of silicon."

It would seem from these statements that Martin had no knowledge of a paper by H. N. Warren, published in the *CHEMICAL NEWS* (lxvi., 113), and also in abstract in the *Journal of the Chemical Society* (1893, lxiv., 11), in the *Ber.* (1893, lxxv.), and doubtless in other journals.

In this paper Warren describes a method for the preparation of silicon tetrachloride with the aid of commercial ferrosilicon (15 per cent Si). The crude material is simply heated in a clay retort in a stream of chlorine. The credit for the discovery of this process is therefore Warren's alone, and Martin's omission of any reference to Warren is all the more remarkable in view of the fact that Warren's method is given not only in the journals mentioned above,

but also in some of the larger works on organic chemistry (Dammer's "Handbuch"), and even in some of the textbooks ("Inorganic Chemistry," Kipping and Perkin).

The author of this note can state from personal experience that Warren's method gives excellent results; it was employed in the author's laboratory more than ten years ago, at a time when silicon tetrachloride was not on the market or else was very much more expensive than it is now. In the course of the preparation of the tetrachloride a considerable proportion of a by-product of higher boiling-point than the tetrachloride was separated; this liquid, however, was not examined, as it was doubtless a mixture of the higher chlorides of silicon analogous to that investigated by Gattermann and Weinlig.

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## AN ELECTROSTATIC BASIS FOR THE LAW OF MASS ACTION IN ELECTROLYTIC SOLUTIONS.

By R. T. LATTEY.

IF in a solution we have two kinds of ions carrying charges of  $+mq$  and  $-nq$  electrostatic units each, and if the concentrations of these ions at any point are represented by  $C_+$  and  $C_-$  per cc., then according to the law of mass action,  $C_+nC_-$  is a constant multiple of the concentration of the undissociated molecules. The ordinary derivation of this law is from analogy to equilibria studied experimentally in gaseous systems and in solutions of non-electrolytes, but the extension of such laws to electrolytic solutions leaves room for doubt as to how far electrical conditions may render the analogy valueless.

Let us suppose that a charged sphere is introduced into such a solution. It will repel the ions of like charge and attract those carrying charges of the same sign as its own.

Consider the conditions on a spherical shell of radius  $x$  having the charged sphere at its centre. Let the total charge inside the shell due both to the sphere and to the ions of both kinds be equal to  $Q$  positive units.

The number of ions in unit area of the shell will be be  $C_+dx$  and  $C_-dx$ , and if  $k$  is the dielectric constant of the medium the forces per unit area due to electrostatic repulsion will be—

$$mqC_+dxQ \div kx^2 \text{ and } -nqC_-dxQ \div kx^2.$$

If in crossing this shell the concentrations change by  $dC_+$  and  $dC_-$  there will exist osmotic pressures of—

$$PdC_+ \div N \text{ and } PdC_- \div N;$$

where  $N$  = the number of molecules in 1 cc. of gas under pressure  $P$  dynes per sq. cm.

If there is to be equilibrium these osmotic pressures must balance the electrostatic pressures; hence, for the positive ions,—

$$mqC_+QNdx = kx^2PdC_+,$$

and for the negative ions—

$$-nqC_-QNdx = kx^2PdC_-.$$

By dividing one equation by the other we get—

$$mC_+dC_- = -nC_-dC_+,$$

and on integration—

$$C_+nC_- = K \text{ (a constant).}$$

Since the undissociated molecules have no electric charge their distribution will be unaffected by the disturbing charge, and will therefore be the same throughout the solution. At considerable distances from the disturbing charge  $C_+$  and  $C_-$  will have practically constant

values ( $C_+$ ) and ( $C_-$ ), and it is clear from the nature of the chemical origin that  $n(C_+) = m(C_-)$ .

Hence,  $K = (C_+)^m + n(n/m)^m$ ; i.e.,  $K$  depends on the actual concentration in the absence of a disturbing charge. This is in agreement with the law of mass action according to which  $K$  is a constant multiple of the concentration of undissociated molecules.

By applying similar reasoning to cases where several kinds of ions are present it may be shown that the equilibrium between each pair of positive and negative ions is unaffected by the presence of the others.

243, Woodstock Road, Oxford,  
February 27, 1915.

## MICRO-PHOTOGRAPHY.

By J. EDGAR HURST.

In a busy iron-works laboratory micro-investigations are very often suppressed by lack of time to do much of the laborious detail in connection with the recording of results. Very often, especially with cast-iron, when examining a series of specimens, records are a much more effective means of comparing the specimens than the memory. The impossibility of taking photographs of each individual specimen of the series is obvious. The usual method is to resort to drawing, using one of the various types of drawing eye-pieces. This method is open to serious objections; first and foremost, the length of time taken, and secondly, the inability of this method to accurately portray anything but what is boldly outlined. For example, the laminated structure of eutectics and the edges of graphite plates are exceedingly difficult to reproduce by this method.

The following method has been successfully used by the author, and has rendered good service in the daily examination of the general structure of cast-iron test bars. The expense and room of plates are saved by its means, and it is well adapted for the busy laboratory. The method is exceedingly simple, and consists in replacing the plate in the dark slide of the camera by a sheet of bromide paper. The thick paper usually known as "Boardoids" or "Cardette" will be found most satisfactory. Should the ordinary paper be used it will be found necessary to cover the paper with a thin glass plate, in order to keep it perfectly flat. The exposure needs to be determined by trial in each individual case, but once determined varies very little, providing of course other factors are kept constant. Using Illingworth's Matte Bromide Cardette, the exposure is very nearly that of the Imperial "Process" plate, and with an 110-volt arc lamp is about 150 sec. The photograph obtained of course is a negative. This is the only apparent disadvantage of the process, but it will be found that on using the process one gets quite accustomed to the reading and examination of these negatives.

This method has rendered great service in the observation and cataloguing of network structures of phosphide eutectic in cast-iron, and undoubtedly it would be of great service in many other instances where a whole series of structural arrangements require to be recorded. For rapid general work it is useful to have a separate camera arrangement, which in the author's case consists of a length of light brass tube, 6" long, 3" diameter, one end being closed by a cap containing a plush-lined brass collar, which fits on the eyepiece of the microscope. The other end is arranged to screw into the dark slide-holding arrangement of an old  $\frac{1}{2}$ -plate camera in such a manner as to allow of the paper being exposed in the ordinary way. Reversing solutions have been tried on the negatives produced in this way, but the results are far from satisfactory. However, in the author's case the negatives give very little trouble, and the time, labour, and expense saved far outweighs any slight disadvantage from this cause.

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## THE CHEMICAL ANALYSIS OF PAPER.

By HENRY ALDOUS BROMLEY.

THE materials entering into the composition of paper in its finished state may be classified as follows:—(1) Fibrous foundation, (2) moisture, (3) mineral matter, (4) sizing materials, (5) colouring matters, (6) substances added for special purposes, (7) chemical residues, &c. Such as the foregoing as admit of quantitative estimation by chemical means are considered in this article.

The two fibrous materials admitting of quantitative estimation with any degree of accuracy are:—(1) Esparto and (2) mechanical wood-pulp.

This process depends on the fact that the acid distillation of an oxycellulose yields furfuraldehyde in direct relation to the amount of fibre present in the paper. The determination is conducted as follows:—A flask is prepared through the cork of which passes a stoppered separating funnel, and having a glass outlet tube connected with a Liebig's condenser. In the flask is placed 5 grms. of the paper to be examined, cut into small pieces, and 100 cc. of hydrochloric acid of specific gravity 1.06. The flask is then heated in such a manner that 2 cc. of distillate per minute are delivered, a graduated measure being used for its collection. When the distillate reaches 30 to 40 cc. it is removed to a flask, and two or three further portions collected in the same way. As each portion of distillate is removed from the collecting measure a corresponding further amount of hydrochloric acid is added to the distilling flask. The distillation is continued until a drop of the distillate ceases to give the aldehyde reaction with aniline acetate.

This reaction is obtained by allowing a drop of the last portion of distillate to fall from a glass rod into a solution of aniline acetate acidified with acetic acid in a white basin. In the presence of an aldehyde a rose-red coloration is produced. Failure of the distillate to give the reaction shows that the distillation is complete. The separate portions of distillate are mixed together in a beaker, and the hydrochloric acid present neutralised with a slight excess of sodium carbonate, after which a small quantity of acetic acid is added.

For the precipitation of the furfural a solution is prepared containing 12 grms. of phenylhydrazine and 7.5 grms. of glacial acetic acid in 100 cc. distilled water. This solution is added to the distillate until a drop of the latter ceases to give the aldehyde reaction previously described. The solution is set aside for some hours with occasional stirring for the golden crystalline precipitate of furfural hydrazone formed to separate out, which it does according to the following equation:— $C_5H_4O_2 + C_6H_5N_2H_3 = C_5H_4ON_2HC_6H_5 + H_2O$ .

The precipitate after being washed is filtered off through a weighed Gooch crucible. The crucible and its contents are dried in a current of air at about 60° C., and weighed. The weight of precipitate multiplied by 0.538 gives the weight of furfural. The average yield of furfural from 100 parts of esparto has been shown to be 12.5. The weight of esparto present in the 5 grms. of paper is therefore obtained by multiplying the weight of furfural by 8, whence the percentage weight is easily calculated.

Several methods have been suggested for the determination of ground wood in paper. The best known is probably that of Würster, which depends on the depth of colour produced with di-methyl paraphenylene-diamine. Paper impregnated with this substance can be obtained, together with a scale of colours corresponding to the tints produced by various percentages of mechanical wood. The test paper is moistened and laid between a fold of the paper to be tested. In the presence of mechanical wood the paper is coloured red, and the tint is then compared with the standard colour scale.

The method of Godeffroy and Coulon depends on the property of lignin of reducing a solution of gold chloride to metallic gold. For the estimation a weighed quantity



of paper is torn into small pieces and divided into two portions of equal weight. Each portion is boiled for ten minutes in a 10 per cent solution of ammonia, washed and dried. One portion is now burned and the ash determined. The second portion is treated by boiling with a solution of tartaric acid, followed by extraction with alcohol and ether to remove the size, and is then boiled for a further ten minutes with a 10 per cent solution of gold chloride, being afterwards washed, dried, and finally ashed. On deducting the weight of the ash obtained in the first determination from that obtained in the second, the amount of reduced gold is found. This amount is a measure of the lignone groups present, and therefore of the amount of mechanical wood. The weight of gold multiplied by 4.7 (the average factor obtained from a number of determinations) gives the weight of mechanical wood in the amount of paper taken for analysis.

In the phloroglucin method of Cross, Bevan, and Briggs advantage is taken of the power of ligneous tissue to absorb a solution of standard phloroglucin, the amount of absorption being directly related to the quantity of mechanical wood present. The estimation is carried out as follows:—Two grms. of the paper are pulped, dried at 100° C., and weighed. The weighed pulp is transferred to a dry flask, covered with 40 cc. of a solution made by dissolving 2.5 grms. of pure phloroglucin in 500 cc. of hydrochloric acid of specific gravity 1.06, shaken, and allowed to stand for some hours. The liquid is then filtered through cotton placed in the neck of a funnel, and 10 cc. of the filtrate taken for titration. This 10 cc. is mixed with 20 cc. of hydrochloric acid (specific gravity 1.06), heated to 70° C., and titrated with a standard solution of formaldehyde made by dissolving 1 cc. of 40 per cent formaldehyde solution in 500 cc. of hydrochloric acid (1.06 specific gravity). The aldehyde solution is added from a burette 1 cc. at a time with an interval of two minutes between each addition. A piece of cheap newspaper is used as an indicator, free phloroglucin producing a red stain when a drop of the liquid is allowed to fall on the paper. Toward the end of the reaction it becomes necessary to dry the paper before a Bunsen burner before the stain will appear. Treated in this way one part of phloroglucin in thirty thousand gives a perceptible stain. When no further colour is produced the reaction is complete; 10 cc. of the original phloroglucin solution are now titrated in the same way, the difference between the two results giving the amount absorbed by the lignin. The proportion of mechanical wood in the paper is calculated from the following formula:—

$$H = \frac{100(p - 1.0)}{8 - 1.0}$$

Where H = per cent of mechanical wood.

p = absorption value of the dry ash-free sample.

8 = absorption value of mechanical wood.

1 = absorption value of sulphite wood.

Another method depends upon the action of chlorine gas on lignin. The paper under examination is rendered neutral by first boiling with a weak solution of sodium carbonate, treating with weak acetic acid, and then washing with hot water. It is then exposed in a damp condition to the action of chlorine gas, which enters into combination with the lignin. After the chlorination is complete the excess of chlorine is removed, and a known quantity of water added, and the resulting hydrochloric acid determined by titration with standard soda. Each cc. of normal soda used is said to be equivalent to 0.22 gm. of mechanical wood-pulp.

In practice it is usually only necessary to make a determination of added moisture in paper. For such determination it is best to weigh a whole sheet. Dry this at 100° C. in the oven, and then allow the sheet to cool while freely exposed to the atmosphere of the laboratory. The loss of weight gives the amount of moisture over and above that normally present, and is expressed as a percentage on the weight of the sheet.

One gm. of paper is torn into fragments and incinerated in a weighed platinum crucible, tilted at an angle to allow free access of air. If difficulty is experienced in completely burning off the last charred particles the residue may be moistened with a few drops of ammonium nitrate, and the heating continued. When the ash is almost completely white the crucible is cooled and weighed, and the weight of ash determined by difference. The ash is expressed as a percentage on the weight of paper taken. Where this weight is 1 gm. the weight of ash gives the percentage figure directly, if the decimal point be moved two places to the right. Thus, 0.155 gm. = 15.5 per cent.

An alternative method consists in tearing the paper into three or four pieces, and impaling these on the free ends of a piece of twisted platinum-wire let into a glass holder. The incineration process is thus somewhat accelerated.

These may be china-clay, pearl hardening, blanc fixé, talc, and satin-white, either separately or in admixture. Where any one loading is present alone its determination is practically identical with that of the ash, after correction for that normally due to the fibrous material of the paper. In the case of pearl hardening (calcium sulphate) and blanc fixé (barium sulphate) some reduction of the sulphate to sulphide takes place on ignition, and the ash requires moistening with sulphuric acid and re-heating before its weight is determined. Loading materials contain more or less water which is driven off at a red-heat, and this loss should be allowed for in the calculation. Thus pearl hardening normally contains two molecules of water (20 per cent), and china-clay about 12 per cent.

Pearl hardening and satin-white in admixture with other loadings are easily separated from them by reason of their ready solubility in dilute hydrochloric acid. For the determination of blanc fixé, talc, and china-clay the residue after ignition is fused with several times its own weight of fusion mixture in a platinum crucible. By this means the bases are converted into carbonates, while the sulphates and silicates enter into combination with the sodium and potassium of the fusion mixture. The fused mass is treated with hot water for some time to dissolve out the soluble sulphates and silicates, after which the liquid is filtered and the filtrate set aside for determination of the acids. The insoluble residue, which may contain barium, aluminium, and magnesium carbonates, is dissolved in dilute hydrochloric acid, and the solution reserved for determination of the bases.

The filtrate reserved for the determination of the acids as above is acidified with hydrochloric acid, evaporated to dryness, moistened with more hydrochloric acid, heated for a short time on the sand-bath, and the residue taken up with hot water. This causes the separation of silica, which is then filtered off, washed, dried, ignited, and weighed. The filtrate from this last operation is heated to boiling, and sulphates, if present, precipitated with barium chloride in the usual way, filtered, and the precipitate washed, dried, ignited, and weighed.

The solution reserved for the determination of the bases is treated with strong ammonia to precipitate alumina, which latter is filtered off, washed, dried, ignited, and weighed. The filtrate from this last operation is treated with ammonium sulphate to precipitate barium, which is then ignited and weighed as barium sulphate. The final filtrate is evaporated to small bulk, half its volume of ammonia added, then excess of a solution of sodium phosphate, and any resulting precipitate estimated as magnesium pyrophosphate in the usual manner.

These bodies being nitrogenous and containing fairly constant proportions of nitrogen, their estimation resolves itself into a determination of nitrogen. The determination may be made by either of two methods, viz., by combustion with soda-lime or by Kjeldahl's process. The latter, being the simpler and more generally employed process, is the one described here. Kjeldahl's process depends on the fact that when most nitrogenous bodies are heated with

excess of concentrated sulphuric acid their nitrogen is converted into ammonium sulphate, from which the nitrogen may be liberated by treatment with excess of alkali and distilling.

Into a special hard glass flask is introduced from 1 to 2 grms. (according to the probable proportion of gelatin present) of the paper torn into shreds, followed by about 20 cc. of concentrated sulphuric acid (free from nitrous compounds), and 0.5 gm. of red mercuric oxide. The flask is supported by the neck in an inclined position, and gradually heated up to nearly the boiling-point of the acid. At this stage 5 grms. of potassium sulphate are added to raise the boiling-point, and the heating is continued. The liquid is at first black, but becomes lighter in colour as the reaction goes on, passing through brown to yellow, and finally becoming almost colourless.

The reaction usually takes several hours to complete, but once started may safely be left to itself. A crystal of copper sulphate added during the later stages will hasten completion. When the nearly colourless contents of the flask are cold they are diluted with a considerable bulk of water, and transferred to a 500 cc. copper distilling flask, together with enough of a 50 per cent solution of caustic soda to render the liquid alkaline, 20 cc. of a weak solution of potassium sulphide, and one or two pieces of broken clay-pipe stem or pumice. A special bent delivery tube arranged to act as a condenser is used, fitted into the cork of the distilling flask, the other end dipping into a graduated measure containing a known volume (about 20 cc.) of one-tenth normal sulphuric acid.

The liquid in the flask is now rapidly distilled for about half-an-hour, by which time all the ammonia will have come over. Care must be taken so to regulate the heat that neither the liquid in the flask tends to be driven over into the delivery measure nor the acid to be sucked back into the flask. The distillate is cooled, and an aliquot portion titrated with one-tenth normal alkali, using methyl-orange. The number of cc. of alkali required for the whole 20 cc. of acid deducted from 20 gives the number of cc. of acid neutralised by the ammonia. Each cc. of this neutralised acid corresponds to 0.00339 gm. of nitrogen, and the figure thus obtained multiplied by 556 and divided by the weight of paper taken gives at once the percentage of "bone-dry" gelatin present. In the case of casein the factor is 490.

A blank experiment using a paper free from gelatin should in all cases be done side by side with the above for the purpose of testing the reagents, &c. (even the air of the laboratory may invalidate the results by the presence of ammonia). Any neutralisation of acid obtained in the "blank" must be deducted from the figure obtained in the main experiment.

The difficulties in carrying out an accurate determination of rosin in paper are great. Many methods have been proposed, but most of them are more or less unreliable. The simplest is perhaps that based on the turbidity produced on diluting an alcoholic solution of rosin with a considerable bulk of water. The paper under examination is extracted with alcohol, and the extract poured into water in a tall glass cylinder. An opalescent turbidity is produced, due to the precipitation of free rosin, which turbidity is compared with that produced by an alcoholic solution containing a known weight of rosin. The results obtained by this method are very variable, since other bodies liable to be present are precipitated at the same time—notably fatty acids from the soap often used in manufacture. The presence of more than 6 parts of rosin in 100,000 is further said to interfere with the delicacy of the reaction.

In Schumann's method the rosin is extracted by digesting with dilute alkali, precipitated with dilute sulphuric acid, filtered off, washed, dried, and weighed. Owing to the difficulty in completely removing the alkaline resinates formed the method is unsatisfactory, giving low results. The alkali, like alcohol, also extracts other bodies besides rosin.

The following method has been recently proposed by C. F. Sammet, of the Bureau of Chemistry, Washington, who claims the results to be within the experimental error of 0.2 per cent. Five grms. of paper are cut into strips, folded, and extracted in a Soxhlet with acidified alcohol (100 cc. of 95 per cent alcohol with 15 cc. of a 5 per cent solution of acetic acid). The solvent is allowed to syphon over from six to twelve times, after which the alcoholic extract is washed into a beaker, evaporated to small bulk, taken up with 25 cc. of ether, and transferred to a separating funnel containing 150 cc. of distilled water and a little salt to prevent emulsification. The contents of the funnel are well shaken, the water drawn off, and the process repeated. The combined ether extracts are then washed with distilled water to remove water soluble salts, and the washed extract transferred to a platinum dish, the ether evaporated, and the residue dried in the water-oven at 98° to 100° C. for one hour exactly, after which it is cooled and weighed. Fatty and waxy matters removed in the process are in too small proportions to affect the accuracy of the result.

Wurster's method for the determination of starch consists in first extracting rosin by treatment of the paper with absolute alcohol, acidulated with hydrochloric acid, and then drying and weighing the paper. The latter is now boiled with a solution consisting of equal parts of alcohol and water, also acidulated with hydrochloric acid, dried, and again weighed. The difference in the weightings represents the starch present. The method is open to objection for the following reasons, viz.:—Firstly, the alcohol extracts matter in excess of the rosin, and, secondly, the starch is probably never completely removed by any process of simple solution.

The most satisfactory plan yet devised consists in converting the starch into soluble sugars, and then determining these. Two methods are available. In the first, the conversion is effected by means of malt extract or diastase, a weighed quantity of paper being first extracted with alcohol to remove rosin, dried, weighed, and then treated with malt extract at a temperature of about 60° C. for half-an-hour to an hour. The glucose and maltose formed may be estimated directly in the manner hereinafter described, or the paper may be carefully washed, dried, and again weighed, and the difference in the two weightings taken as starch.

The second method depends upon the power of dilute acids to convert starch into glucose. Five grms. of paper are boiled with 500 cc. of distilled water for thirty minutes, and then thoroughly pulped. Sulphuric acid is now added to the liquid in the proportion of 2 per cent of its weight, and the whole is heated on the water-bath under a reflux condenser for three hours, or until the liquid gives no further blue colour with dilute iodine solution. At the end of this time the liquid is filtered, a slight excess of caustic soda added, the filtrate made up to a litre, and 200 cc. taken for the direct estimation of sugar, which may be performed either (1) gravimetrically or (2) volumetrically. Each process is on occasion useful, and both will therefore be described. In each case the reagent used is Fehling's solution, which is prepared by dissolving 34.64 grms. of pure crystallised copper sulphate in distilled water, and diluting to 500 cc., while 70 grms. of caustic soda and 180 grms. of re-crystallised potassium sodium tartrate (Rochelle salt) are dissolved in about 100 cc. distilled water, and the solution also diluted to 500 cc. The two solutions are mixed in equal proportions just before use. From this mixture the reducing sugars possess the power of precipitating red cuprous oxide in proportion to the amount of sugar present.

For the gravimetric estimation, to 20 cc. of Fehling's solution at the boil is added the 200 cc. of filtrate from the acid treatment of the paper, and the whole boiled for a further ten minutes. The red precipitate formed is filtered through a Gooch crucible, washed, ignited, and rapidly weighed as cupric oxide. The weight multiplied by 0.4535 gives the weight of glucose in the 200 cc. of

filtrate. The amount of glucose in the whole litre of filtrate multiplied by 0.9 gives the weight of starch present in the 5 grms. of paper.

For the volumetric estimation, 10 cc. of Fehling's solution diluted with water are boiled in a beaker, and while boiling, the sugar solution, of the same strength as in the gravimetric process, is run in from a burette until the blue colour of the Fehling's solution is completely discharged. In practice it is not easy to determine the end point of the reaction, and it is therefore better to employ an indicator. For this purpose a drop of a solution of potassium ferro-cyanide acidulated with acetic acid is placed on a white tile or spotted on a filter-paper, followed by a drop of the liquid from the beaker. While any un-reduced copper remains in the latter, a brown precipitate or stain will be produced. The number of cc. of sugar solution used is then read off, and will correspond to 0.05 grm. of glucose since this amount is the weight of glucose capable of completely reducing 10 cc. of Fehling's solution. The amount of starch present in the 5 grms. of paper is calculated as follows:—

$$\frac{0.05 \times 1000 \times 0.9}{\text{No. of cc. of sugar sol. used.}}$$

#### Colouring Matters.

*Smalts*, existing as it does in high-class papers, usually without admixture with loading materials, can be estimated with sufficient accuracy by incinerating the paper, weighing the ash, and making a correction for the small proportion of the latter due to the fibre, &c. This proportion does not usually exceed 2 per cent.

The *ultramarines* are of variable and even doubtful composition, and are therefore best estimated by comparing the depth of colour of the ash with that of standard mixtures of the pigment with known proportions of china clay.

*Chrome yellow, orange, &c.*, also of variable composition, may be determined, if necessary, by estimating the lead and chromium separately, and calculating the results to the nearest indicated composition. It is scarcely necessary here to describe the full gravimetric process as it is likely to be but rarely required. It will be sufficient to say that the lead is precipitated and estimated as the sulphate, and the chromium as chromic oxide.

*Prussian blue* may be determined approximately by estimating the iron by igniting the paper, fusing the ash with sodium carbonate, treating the fused product with hot water, filtering, and boiling the residue with dilute hydrochloric acid and a drop or two of nitric acid. The solution is then again filtered, and the iron and alumina precipitated with ammonia in the presence of a little ammonium chloride. The precipitate of iron and aluminium hydrates is washed, filtered off, and digested with excess of caustic soda, then filtered again and carefully washed. The residue, which consists entirely of iron, is washed, dried, ignited, and weighed as the oxide. This process also serves for the estimation of all other iron pigments except the natural colours, ochres, &c.

*Oils and fats* can be estimated by extracting with ether, evaporating the solvent, and weighing the residue.

*Paraffin-wax*, similarly to the above, using benzene or or petroleum spirit.

*Salicylic Acid*.—This substance is used as a preservative in papers required for wrapping foodstuffs. It is extractable with petroleum ether, and may be estimated in the solution by diluting the latter with an equal volume of 95 per cent alcohol and titrating with one-tenth normal alkali, using phenolphthalein as indicator. Each cc. of one-tenth normal caustic soda is equivalent to 0.0138 grm. of salicylic acid.

*Carbolic Acid*.—The estimation of carbolic acid in carbonised wrapping paper is frequently required. Commercial carbolic acid consists chiefly of cresylic acid with higher phenols, but little real phenol being usually present. Since, however, cresol is probably as efficient an anti-

septic and insecticide for ordinary purposes as phenol, the absence of the latter body is of little importance. Carbolic acid may contain tar oils, which are, however, quite inert. Naphthalene is also liable to be present.

For the estimation of commercial carbolic acid the bromine absorption method in use for the determination of phenol is valueless. The writer has found the following method, which is based on a process originally described by Muter, quite satisfactory:—

From 10 to 20 grms. of paper (according to the probable proportion of acid present) are cut into pieces and extracted with a sufficient quantity of alcohol (95 per cent) in a Soxhlet. The extract is transferred to a basin, mixed with about half its volume of a 10 per cent solution of caustic soda, and the mixed liquids evaporated in the water-bath to small bulk. Tar oils and naphthalene, if present, here separate out and may be removed by filtration. The liquid is now transferred to a separating funnel and hydrochloric acid added cautiously and with gentle shaking until the liquid shows an acid reaction. Means should be taken to prevent the mixture becoming too hot during the process. A little brine is now added. The liberated tar acids rise to the surface of the liquid, which also becomes milky from the precipitation of rosin. The whole is now set on one side for a short time to complete the separation of the layer of tar acids, after which the resinous liquid is drawn off as completely as possible. The residue of oil is shaken up with ether or petroleum spirit, transferred to a weighed flask, the solvent evaporated off, and the residue weighed.

*Bleach Residues*.—Excessive quantities of chlorides are the chief indications of faulty treatment of bleach residues and of insufficient washing. For the estimation of soluble chlorides the paper is extracted with hot distilled water and the solution evaporated to small bulk. To the resulting liquid is added, while stirring, silver nitrate solution till no further precipitate occurs, followed by a little nitric acid. The precipitate is allowed to settle, and the clear liquid is decanted through a filter. The bulk of the residue is now carefully washed several times with boiling distilled water to free it from acid, and is finally collected on the filter, and the whole dried in the water oven. The chloride is scraped from the filter, transferred to a weighed crucible, and heated at a low temperature until it commences to fuse. The filter is ashed separately on the crucible lid, and the ash treated with a drop of *aqua regia*, the resulting chloride being dried and added to the residue in the crucible. The weight of chloride multiplied by 0.248 gives the total chlorine.

*Alum*.—For the estimation of alum the paper is extracted with hot water, rendered slightly acid with a drop or two of sulphuric acid. The alumina is then precipitated with ammonia and estimated as described under "Loadings."

*Acidity*.—The total acidity of a paper is estimated by titrating a distilled water extract with one-tenth normal alkali, using litmus as indicator.

*Soluble Sulphur Compounds* are determined by extraction with distilled water and titration with one-tenth normal iodine solution.

*Arsenic*.—An estimation of this substance is occasionally required, as where it forms the base of a colouring matter, or as in fly-papers, &c. Where a relatively large quantity is available and is present as arsenious acid (as it frequently is) it may be estimated by extracting with a boiling solution of sodium bicarbonate and titrating the extract with one-tenth normal iodine and starch. Each cc. of one-tenth normal iodine corresponds to 0.0049 grm. of arsenious acid. Where minute quantities of arsenic only are present (or available) the following process is necessary:—

The paper is first heated for some time with a mixture of sulphuric and nitric acids in the proportion of 30 parts to 1. The carbonised residue is boiled with distilled water and filtered. An apparatus is prepared consisting of a flask provided with a stoppered funnel and having an outlet connected to a drying tube containing calcium chloride,

and leading to a hard-glass tube having a piece of wire gauze wrapped round it near the middle, and heated by a Bunsen under the gauze. The arsenic extract is introduced into the flask via the stoppered funnel after 2 to 3 grms. of arsenic, free zinc, and some pure hydrochloric acid have been placed in the flask. A mixture of arseniuretted hydrogen and hydrogen is evolved, which is split up on reaching the heated portion of the tube and deposits a mirror of metallic arsenic in the cooler portion of the tube. This mirror is compared with those produced by solutions containing known amounts of arsenic. A "blank" experiment must always be performed in order to test the purity of the reagents.—*Chemical Engineer*, xx., No. 6.

### THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.\*

By O. L. BARNEBEY.

(Continued from p. 126).

#### *Application of other "Preventives" (continued).*

MAGNESIUM sulphate and zinc sulphate produce decided effects in checking the influence of hydrochloric acid, the former being more efficient than the latter.

Scrutiny of Table XI. shows good results in only two cases when magnesium sulphate was used, *e.g.*, Experiments 2 and 3, in which only 5 cc. of hydrochloric acid was added. In the zinc sulphate series all the results were too high. Almost identical volumes of permanganate were required for 5 cc. of hydrochloric acid within a range of 25 to 200 cc. of the zinc sulphate solution. A somewhat analogous set of figures was obtained for 10 cc. of hydrochloric acid within a range of 50 to 200 cc. of the magnesium sulphate. These results show a tendency toward prevention, which, nevertheless, is not sufficient for practical application in titrating iron.

Chromium and ferric sulphates were found to have no value as preventives of the high results due to the action of hydrochloric acid on permanganate. High concentrations of chromium were naturally impossible on account of the colour imparted to the solution.

Mixtures of tri-potassium or di-sodium phosphate and phosphoric acid were found to produce excellent prevention.

Experiments 1, 2, 3, 24, 25 are titrations with "manganese sulphate solution No. 1." Experiments 8, 10, 14, show the influence of adding the alkaline phosphate before the acid. In all likelihood some of the iron is precipitated as ferrous phosphate in these cases, yielding low results. Experiments 16, 19, 20, indicate an insufficiency of acid to keep the ferrous phosphate from forming. Experiments 12, 13, 15, 21, 22, show that when the proper adjustment of phosphoric acid and potassium phosphate is obtained correct results follow. A proportion of not less than three volumes of 1-1 phosphoric acid to one volume of 50 per cent  $K_3PO_4$  gives the best results. A solution containing 500 grms. of tripotassium phosphate (or its equivalent in dipotassium phosphate) and 1500 cc. of phosphoric acid (sp. gr. 1.7) diluted to 2 litres can be used instead of the separate reagents. Twenty cc. of this solution will stop the action of 5 cc., and 60 cc. will suffice for 25 cc. of hydrochloric acid (sp. gr. 1.10).

In Series XIII. a saturated solution of  $Na_2HPO_4 \cdot 12H_2O$  was employed.

This series shows excellent prevention, even 35 cc. of hydrochloric acid being taken care of nicely, and 50 to 100 cc. did not produce an error such as one might anticipate.

The phosphoric acid and sodium phosphate may be combined into one solution by preparing as follows:—Solution of 500 grms. of disodium phosphate in 1000 cc.

TABLE XI.

Series XIII.—Magnesium and Zinc Sulphates as Preventives. 1 cc.  $KMnO_4 = 0.004847$  gm. Fe. 20 cc.  $FeCl_3 (= 0.2283$  gm. Fe) + 10 cc.  $HgCl_2$  taken.  $MgSO_4$  solution =  $MgSO_4 \cdot 7H_2O = 500$  grms. per litre.

Expt. No.	HCl. Cc.	$MgSO_4$ Cc.	Fe found. Grms.
1.	5	—	0.2283 (a)
2.	5	50	0.2283
3.	5	50	0.2285
4.	10	50	0.2293 (b)
5.	10	100	0.2297
6.	10	150	0.2293 (b)
7.	10	200	0.2293 (b)
8.	15	50	0.2297 (b)
9.	20	50	0.2327 (b)
10.	25	50	0.2346 (b)
11.	10	—	0.2366 (c)

1 cc.  $KMnO_4 = 0.005309$  gm. Fe. 20 cc.  $FeCl_3 (= 0.2283$  gm. Fe) + 10 cc.  $HgCl_2$  taken.  $ZnSO_4$  solution = 500 grms.  $ZnSO_4 \cdot 7H_2O$  per litre.

1.	5	—	0.2283 (a)
2.	5	—	0.2378
3.	5	20	0.2296
4.	5	25	0.2293
5.	5	50	0.2293
6.	5	100	0.2293
7.	5	200	0.2291
8.	25	100	0.2325 (c)
9.	25	200	0.2304 (b)
10.	10	50	0.2293
11.	15	50	0.2309
12.	15	100	0.2393
13.	20	125	0.2309
14.	20	200	0.2309
15.	20	250	0.2291

(a) 20 cc. Mn solution No. 1 added.

(b)  $HgCl$  partially disappears.

(c)  $HgCl$  disappears entirely.

TABLE XII.

Series XIV.—Potassium Phosphate Mixtures as Preventives.  $K_3PO_4$  solution = 500 grms.  $K_3PO_4$  per litre. 20 cc.  $FeCl_3 = 0.2031$  gm. Fe + 10 cc.  $HgCl_2$  taken. 1 cc.  $KMnO_4 = 0.004887$  gm. Fe.

Exp. No.	HCl. Cc.	$H_3PO_4$ Cc.	$K_3PO_4$ Cc.	$H_2SO_4$ Cc.	Weight of Fe found.
1.	5	—	—	—	0.2031 (a)
2.	5	—	—	—	0.2028 (a)
3.	5	—	—	—	0.2031
4.	5	—	—	—	0.2055
5.	10	—	—	—	0.2160 (b)
6.	25	—	—	—	0.2189 (b)
7.	50	—	—	—	0.2180 (b)
8.	5	—	10	30	0.1906 (c)
9.	5	—	10	30	0.2048
10.	5	—	10	30	0.1899 (c)
11.	5	—	10	30	0.2053
12.	5	30	10	—	0.2031
13.	5	30	10	—	0.2033
14.	5	30	10	—	0.1891 (b)
15.	10	30	10	—	0.2031
16.	5	30	20	—	0.2004
17.	25	30	10	—	0.2072
18.	25	50	20	—	0.2051
19.	25	50	30	—	0.2009
20.	25	75	30	—	0.2026
21.	25	100	30	—	0.2031
22.	25	200	30	—	0.2031
23.	25	200	—	—	0.2063
24.	5	—	—	—	0.2031
25.	5	—	—	—	0.2033

(a) 30 cc. manganese solution No. 1 added.

(b)  $HgCl$  dissolved almost completely.

(c) Added  $K_3PO_4$  before the acid ( $H_3PO_4$  or  $H_2SO_4$ ) + 50 cc. manganese solution No. 1 added.

\* From the *Journal of the American Chemical Society*, xxxvi., No. 7.

TABLE XIII.

Series XV.—Disodium Phosphate Mixtures as Preventives.  
20 cc.  $\text{FeCl}_3 = 0.2280$  grm.  $\text{Fe} + 10$  cc.  $\text{HgCl}_2$  taken.  
1 cc.  $\text{KMnO}_4 = 0.004887$  grm.  $\text{Fe}$ .

Expt. No.	HCl. Cc.	$\text{Na}_2\text{HPO}_4$ Cc.	$\text{H}_3\text{PO}_4$ Cc.	Weight of Fe found.
1.	5	50	100	0.2280
2.	10	50	100	0.2280
3.	15	50	100	0.2284
4.	20	50	100	0.2282
5.	25	50	100	0.2280
6.	30	50	100	0.2280
7.	35	50	100	0.2282
8.	50	50	100	0.2292
9.	60	50	100	0.2292
10.	100	50	100	0.2292 (b)
11.	5	5	10	0.2287
12.	5	10	20	0.2280
13.	5	20	40	0.2278
14.	5	20 (a)	—	0.2280

(a) Manganese solution No. 1.  
(b) End-point unstable.

TABLE XIV.

Series XVI.—Cerium Sulphate as Preventive. 20 cc.  $\text{FeCl}_3 (= 0.2291$  grm.  $\text{FeCl}_3) + 10$  cc.  $\text{HgCl}_2$  taken.  
1 cc.  $\text{KMnO}_4 = 0.004887$  grm.  $\text{Fe}$ .

Expt. No.	HCl. Cc.	$\text{Ce}_2(\text{SO}_4)_3$ solution. Cc.	Weight of Fe found.
1.	5	10	0.2309
2.	5	20	0.2291
3.	5	20	0.2293
4.	5	20	0.2293
5.	10	20	0.2299
6.	7	20	0.2293
7.	5	25	0.2293
8.	5	35	0.2288
9.	5	50	0.2288
10.	5	20 (a)	0.2291

Series XVII.—Cerium Sulphate Mixture as Preventive (d).  
20 cc.  $\text{FeCl}_3 (= 0.1571$  grm.  $\text{Fe}) + 10$  cc.  $\text{HgCl}_2$  taken.  
1 cc.  $\text{KMnO}_4 = 0.004887$  grm.  $\text{Fe}$ .

1.	5	5	0.1583
2.	5	10	0.1570 (b)
3.	5	10	0.1579 (c)
4.	5	15	0.1572 (c)
5.	5	25	0.1572 (c)
6.	10	20	0.1574 (b)
7.	20	20	0.1614 (c)
8.	20	35	0.1572
9.	5	20 (a)	0.1571

(a) Mn solution No. 1.

(b) Slow titration.

(c) Rapid titration.

(d) A solution of mixed earth sulphates when analysed was found to contain 65 grms.  $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} + 200$  cc.  $\text{H}_2\text{SO}_4$  per litre. This solution was used as was the cerium sulphate of the preceding series.

of phosphoric acid and 500 cc. of water, then dilution to 2000 cc. Thirty cc. is a sufficient quantity for 10 cc., and 100 cc. are enough to offset the action of 25 cc. of hydrochloric acid.

Cerium sulphate gives excellent prevention of the hydrochloric acid interference. In fact, it works as effectively as manganous sulphate when its efficiency is measured on the basis of grm. equivalents. Twenty grms. of  $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  were dissolved in 250 cc. of water to be used in Series XVI. and XVII.

Thus it is to be seen that  $\text{Ce}_2(\text{SO}_4)_3$  is very effective in stopping the detrimental nature of hydrochloric acid on permanganate, its value being commensurate with  $\text{MnSO}_4$ .

(To be continued).

## MOBILISATION OF INDUSTRY AND SCIENCE.

CONFERENCE AT MANSION HOUSE.

A GREAT deal has been written of late about the co-operation of industry with science, but it has not been generally known that a considerable amount of quiet but effective work has been going on during the last five months to consummate that very desirable object.

There are a certain number of people who hold the view that any organisation work of a business nature should be held in abeyance until the war is over, but they forget that there are two wars now progressing, one industrial and the other military.

The phrase "Mobilisation of Industry," which has recently been used, originated at the Institute of Industry and Science, but since the inaugural meeting, held at the Savoy Hotel last October, the phrase has now been altered to that of "Mobilisation of Industry and Science."

To defer the organisation of industry and science until the war is over would lose to us the advantage which our brave troops are creating for us at the front; not only that, but such an organisation could be of considerable assistance to the Government if its services were required.

The arrangements which the Institute of Industry and Science have been making for some months past with regard to the holding of a Conference in London of the leaders of industry and science to discuss the British position have now been completed, and a Conference is being held at the Mansion House on the 25th inst., which the Lord Mayor, who is a Vice-Patron of the Institute, has very kindly placed at the disposal of the Court of Directors. Important speeches will be made by many of our most eminent men of industry and science, and the proceedings will be opened with an address on "The Influence of Science on Political Economy," to be followed by a discussion on "The Co-operation of Science and Industry." The titles may seem somewhat technical, but it may safely be assumed that the discussion will follow essentially practical lines, and will be easily understood by all of those who may be present.

Invitations have already been issued to the trade organisations and leading men of industry, and, most important of all, to our leading men of science, and the proceedings promise to be of a highly interesting nature.

A very effective organisation has already been created by the Institute of Industry and Science, and at a meeting of the directors held on the 10th inst. it was resolved to place the organisation at the disposal of the Government without reservation, and this has already been done.

The gentlemen who are actively engaged in the work of the Institute are as follows:—

- Sir Robert Balfour, Bart., M.P. (Messrs. Balfour, Williamson, and Co., City merchants).
- Sir William Beardmore, Bart. (Chairman, Messrs. Wm. Beardmore and Co., Ltd., Glasgow).
- Alfred Allen Booth, Esq. (Chairman, the Cunard Steam-Ship Co., Ltd.).
- Sir Clifford J. Cory, Bart., M.P. (Messrs. Cory Bros. and Co., Ltd., Cardiff).
- Arthur Du Cros, Esq., J.P., M.P. (Vice-Chairman and Managing Director, the Dunlop Rubber Co., Ltd., London).
- Sir James Heath, Bart. (Messrs. R. Heath and Sons, Ltd., ironmasters, Staffordshire).
- G. B. Hunter, Esq., J.P., D.Sc. (Chairman, Messrs. Swan, Hunter, and Wigham Richardson, Ltd., Wallsend-on-Tyne).
- Claude Johnson, Esq. (General Managing Director, Rolls Royce, Ltd., London and Derby).
- Sir Norman Lockyer, K.C.B., LL.D., F.R.S., &c.
- William Lorimer, Esq. (Chairman, the North British Locomotive Company; Chairman, the Steel Company of Scotland).
- J. Taylor Peddie, Esq., F.S.S.
- Sir William Ramsay, F.R.S., F.C.S., D.Sc., &c.



Sir Boverton Redwood, Bart., F.R.S.E., A.I.C.E., M.I.M.E., &c.

Sir Adolph Tuck, Bart. (Chairman, Messrs. Raphael Tuck and Sons, Ltd.).

J. Turner, Esq. (Chairman, Messrs. Read, Holliday, and Sons, Ltd., Coal Tar Dye Manufacturers).

Sir William George Watson, Bart. (Chairman, Maypole Dairy Company).

George A. Wills, Esq. (Chairman, Imperial Tobacco Company of Great Britain and Ireland).

Sir Herbert H. Bartlett, Bart. (Institute of Builders).

Louis Evans, Esq. (Chairman, John Dickenson and Co., Ltd., President, Papermakers' Association of Great Britain and Ireland).

Sir George Pragnell (Chairman, the Wholesale Textile Association).

Frank Warner, Esq. (President, Silk Association of Great Britain and Ireland).

G. H. Cooper, Esq. (Director, William Lawrence and Co., Ltd.; Chairman, National Federation of Furniture Manufacturers, Ltd.).

Walter Deakin, Esq. (Vice-Chairman, the Machine Tool and Engineering Association, Ltd.).

Thomas C. Moore, Esq., J.P. (The Potteries Industry, Stoke-on-Trent).

A. S. Esselmont, Esq. (Teesside Industrial Development Association).

G. McLaren Brown, Esq. (of the Canadian Pacific Railway).

Moreton Frewen, Esq., J.P. (Brede Place, Sussex).

S. Roy Illingworth, Esq., A.R.C.Sc., A.I.C., B.Sc.

The Hon. Sir John Taverner, K.C.M.G.

The Right Hon. Lord Avebury is Honorary Treasurer of the Institute.

It will be seen that a large number of the principal trade organisations are fully represented in the above group, and also many of our most eminent men of science and industry.

A very important work, entitled "A Study of the First Principles of Production and the Relation of Science to Industry," has been in course of preparation for the last six months, and has now been completed, and will be published next Wednesday prior to the Conference, so that all who are interested in the subject may study the question before the Conference.

The book is by J. Taylor Peddie, F.S.S., with special essays by Sir Norman Lockyer, K.C.B., F.R.S., S. Roy Illingworth, A.R.C.Sc., A.I.C., B.Sc., and others, and is an admirable symposium dealing with the working conditions surrounding British industry, and suggests a new basis. The book will be published by Messrs. Longmans, Green, and Co.

Attendance at the Conference at the Mansion House is by invitation only.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, March 4, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"A Bolometric Method of Determining the Efficiency of Radiating Bodies." By Prof. W. A. BONE, F.R.S., Prof. H. L. CALLENDAR, F.R.S., and H. J. YATES.

In view of the increasing uses of incandescent surfaces in heating operations of all kinds, the authors have investigated, as a scientific problem, the measurement of radiant efficiencies of such surfaces by a bolometric method, which can be standardised by direct comparison with a radiobalance, and which the authors propose to substitute for

the existing water-radiometer-cum-thermopile method (known as the "Leeds Method") used hitherto.

The paper describes the construction and use of a new bolometer, specially designed for the purposes in view, in which the radiation from an incandescent surface, falling on a blackened coil of platinum wire, can be determined in absolute units for the increase in the electrical resistance of the receiving coil, the area of which is sufficiently small to allow of the instrument being standardised from a source of known intensity. And, by way of example, the application of the method to the measurement of both the absolute radiation of a gas fire and its "distribution factor" is described and discussed.

The new method is not only in every way more accurate and reliable, but is also more rapid than the old, and has the further great advantage that if necessary it can be made automatic, and therefore independent of the "personal" error of an individual operator by the use of a recording device.

"The Simplification of the Arithmetical Processes of Involution and Evolution." By E. CHAPPELL.

An arithmetical process can be said to be completely simplified when it is reduced to either addition or subtraction. The invention of logarithms completely simplified multiplication and division, but involution and evolution were only replaced by multiplication and division, so that these processes may still be laborious even with the use of logarithms.

The paper describes a table of the logarithms of the logarithms of numbers recently compiled, by the use of which involution and evolution are also completely simplified. The frequency with which fractional indices, positive and negative, occur in most branches of modern experimental science gives rise to the hope that the tables in question will accomplish for the modern scientist what logarithms did for the scientist of the seventeenth century.

The difficulty of constructing and using such a table is pointed out, but a method of using red and white pages is given by which this difficulty is entirely removed.

The properties of these logarithms of logarithms are discussed at some length, and rules are given for their practical use.

The necessity for a systematic nomenclature is relied on as the justification for introducing new names. It is proposed that the logarithm of the logarithm of a number should be called the "Lolog" of that number.

The paper is accompanied by a complete set of examples showing how the tables should be used in order fully to derive the advantages of the colour system.

Specimen pages are given of the seven tables described.

"The Elastic Properties of Steel at Moderately High Temperatures." By F. E. ROWETT.

The difference in the behaviour of hard-drawn steel tubes, before and after annealing, under stress, led to the experiments described in the paper. At a suitable temperature a hard-drawn tube, which contains a good deal of amorphous material, behaves like a viscous fluid—that is, it flows more or less freely under stress, whereas, at the same temperature, an annealed tube being crystalline will flow in a much less degree, corresponding to the small amount of amorphous material in it.

At a temperature of about 300° C. a hard-drawn tube shows properties similar to those of pitch at ordinary temperatures or of glass at a temperature rather below its softening point. It is still highly elastic under rapidly varying stress, but flows perceptibly when the stress is applied for a long time. On the other hand, in the annealed tube at 300° C. the energy dissipated in a cycle of stress is still almost independent of the time taken over cycle.

At a higher temperature, for example at 540° C., the hard-drawn tube flows rapidly and continues to flow for a long period, though at a diminishing rate, under a shear stress of less than one ton per square inch. Moreover,

like pitch or glass, the steel at this temperature shows considerable elastic afterworking. If the stress be suddenly removed the immediate elastic recovery is followed by a slow backward flow, which persists for many minutes.

*"The Laws of Series Spectra."* By Prof. J. W. NICHOLSON.

The paper contains a critical analysis of the Diffuse, Sharp, and Principal series of Helium, especially in the light of recent interferometer measurements of the leading lines of these series.

The investigation depends on a mode of accurate calculation of the limits of series, not dependent on the type of formula used.

The limits of series with many lines, for which a Hicks formula is already known, can be calculated with extreme accuracy by a new method.

Interferometer measures of leading lines of Helium series enable the best form of the series to be obtained. This form is an extension of that of Rydberg, dependent on  $m + \mu$  and not  $m$ .

The value of Rydberg's constant  $109679 \cdot 2$ , given by Curtis for Hydrogen, is the true value for the arc spectrum of Helium, and is in fact a rigorous constant for arc spectra. Spark spectra are not treated.

The Rydberg-Schuster law of limits is exact for Helium.

It seems probable that  $\mu$  is a simple fraction whose denominator is a multiple of 5, as Halm has suggested. It is exactly  $0 \cdot 7$  for the short series of Helium.

## SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 3, 1915.

Mr. A. CHASTON CHAPMAN, President, in the chair.

MR. David Mitchell was elected a member of the Society. Certificates were read for the first time in favour of Messrs. Paul Seidelin Arup, 31, St. Petersburg Place, Bayswater, W.; Alexander Scott Dodd, 20, Stafford Street, Edinburgh; Harri Heap, Brunside, Lyndhurst Road, Withington, Manchester; Francis Howard Carr, Edgmont, Derby Road, Nottingham.

The following papers were read —

*"Soluble Chlorides and Total Chlorides in some English Cokes."* By STANLEY W. BRIDGE, B.Sc., F.I.C.

An examination has been made of a number of samples of coke derived from English coals and cannels from different districts, with the object of determining the amount of soluble chlorides and total chlorine. The results show that very considerable variations occur in the amounts, and that the variations are, in general, of the same order as in the coal. The proportion of the chlorine remaining in the coke depends, however, also to a large extent on the temperature at which the coal has been carbonised; the coke obtained from the same coal by low temperature carbonisation being much higher both in soluble chlorides and total chlorine than that obtained at a high temperature.

*"Routine Detection and Estimation of Boric Acid in Butter."* By HERBERT HAWLEY, M.Sc., F.I.C.

The paper describes a method for the estimation and detection of boric acid in butter colorimetrically with alcoholic extract of turmeric. The method has the advantage that—(1) the same 20 gm. portion serves for both the detection and estimation of the preservative and for an examination of the constants of the fat; (2) the process yields very rapid quantitative and qualitative results when dealing with a number of samples.

*"Structure of Pepper: Some New Features."* By T. E. WALLIS, B.Sc., F.I.C.

A description with illustrations of the microscopical structure of the seed coat and adjacent layers of the fruit

of *Piper nigrum*, L., with special reference to the modifications found at the apex and the base of the fruit. The tissues described are so greatly altered in these parts that anyone acquainted with their appearance and noticing them in a sample of commercial pepper would be inclined to fancy that some extraneous substance was present, especially as there has hitherto been no complete description of them published.

*"Occurrence of Chlorine in Coal."* By A. DE WAELE.

A case of abnormal corrosion of the tube of an economiser was traced to the presence of chlorine in the coal used, whilst comparisons of total chlorine as determined by combustion in lime and chlorine as soluble chlorine by extraction of the powdered coal with water showed good agreement, averaging about  $0 \cdot 22$  per cent Cl. These coals being traced to their origin of Midland coals from the brine districts, Welsh coals supplied to another boiler, where corrosion was merely normal, were found to average  $0 \cdot 020$  per cent Cl, the ignition and extraction analysis, moreover, agreeing.

## NOTICES OF BOOKS.

*Muter's Short Manual of Analytical Chemistry.* Edited by J. THOMAS, B.Sc.(Lond.). Tenth Edition. London: Baillière, Tindall, and Cox. 1915.

THIS book contains a very complete course of practical work for students of pharmacy. Qualitative analysis, including the detection and separation of common metals, acid radicles, the alkaloids, and organic substances used in medicine, is the subject of the first part of the book, while Part II. treats of volumetric and gravimetric work. Some food analysis is included, simple and direct methods of testing butter, milk, bread, flour, &c., being explained. Special processes used in the analysis of drugs are also given. In the tenth edition many additions and alterations have been made, chiefly such as have been necessitated by changes in the British Pharmacopoeia, and in some other respects the text has been revised.

*A First Course of Practical Chemistry for Rural Secondary Schools.* By WILLIAM ALDRIDGE, B.A., B.Sc. London: G. Bell and Sons, Ltd. 1915.

THIS two years' course in elementary practical chemistry is intended to give the student some training and practice in fitting up and using chemical apparatus, in the description of simple experiments, and the drawing of correct conclusions from observations, which apply chiefly to substances which the average boy in a country secondary school would be likely to come across in his every-day life. The experiments described are mostly easy to perform and require no complicated apparatus, and although the treatment of the subject might appear to some extent superficial and rather desultory the boys' interest would certainly be aroused more than by a mere rigid course in pure chemistry. The section on biological chemistry in particular contains some very instructive experiments.

*Practical Heat, Light, and Sound.* By T. PICTON, M.A., B.Sc. London: G. Bell and Sons, Ltd. 1915.

THIS is a really excellent book for beginners, and a valuable course of work in heat, light, and sound could be based upon it. The directions for the performance of the experiments are always models of clearness and conciseness, and the experiments themselves are well chosen. Many questions are interpolated through the book, and if the author's advice is followed and the pupil is made to answer them in full, the possibility of heedless mechanical work, in which principles are only half understood, will be altogether excluded. Supplementary problems and ques-

tions are also given, and some simple arithmetical calculations. The book may confidently be recommended to the notice of teachers of physics in secondary schools.

*University College of North Wales Calendar for the Session 1914-15.* Manchester: J. E. Cornish, Ltd. 1914.

THE Calendar of the University College of North Wales for the Session 1914-15 contains a short history of the foundation of the University, and full information as to syllabuses, courses of work, regulations, fees, &c. The entrance scholarship examination papers are included, and intending students and those who are interested in university education in Wales will find the Calendar very useful.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 6, February 8, 1915.

**Preparation of some Ether Salts.**—F. Bodroux.—By slowly distilling a mixture of formic acid, ethyl alcohol, and water, ethyl formate is obtained. The yield of ether salt varies with the experimental conditions; if the proportions of acid and alcohol are constant it depends upon the quantity of water employed. As a catalyst formic acid in this etherification is inferior to picric or oxalic acids. By the distillation of a mixture of alcohol with an aqueous solution of hydrobromic acid only a poor yield of volatile ether salt is obtained if the solution of hydrobromic acid is dilute. If instead of  $\text{HBr} \cdot 5\text{H}_2\text{O}$  a mixture of this hydrate and sulphuric acid is used a very good yield of hydrobromic ether is obtained.

**Diagnosis of Glycerophosphoric Mono-ethers.**—L. Grumbert and O. Bailly.—The  $\alpha$ - and  $\beta$ -glycerophosphoric ethers can be distinguished by subjecting them to the action of oxidising agents such as bromine water. In the absence of all hydrolysis only the  $\alpha$ -ether can give a substance of general formula  $\text{RCOCH}_2\text{OH}$ , which can be characterised by Denigès' reactions. Applying this to the crystallised sodium glycerophosphate prepared by Poulenc's method the authors have shown that it is the sodium salt of  $\beta$ -monoglycerophosphoric ether.

*Bulletin de la Société Chimique de France.*

Vol. xv.-xvi., No. 21—24, 1914.

**Action of Chlorinated Solvents upon Hard Copals.**

—Ch. Coffignier.—The author has investigated the actions of di-, tri-, and perchlorides of ethylene, and of tetra- and pentachlorides of ethane upon Zanzibar, Madagascar, and Demerara copals, and has found that the proportions of insoluble matter are as follows:—

	Zanzibar.	Madagascar.	Demerara.
Ethylene dichloride ..	78.70	70.90	70.50
Ethylene trichloride ..	83.20	70.80	79.20
Ethylene perchloride ..	79.20	88.20	64.20
Ethane tetrachloride ..	66.50	37.80	48.70
Ethane pentachloride ..	78.40	63.00	53.10

The action of ethane tetrachloride provides a means of distinguishing Madagascar from Zanzibar and Demerara copals. If boiling is not continued too long only the Madagascar variety gives a solution which appears to be nearly complete in the warm.

**The "Little Journal."**—The December number of this Journal, which is published occasionally by Messrs. Arthur D. Little, Inc., Chemists and Engineers, of Boston, contains some statistical data relating to the effect of the war upon the export and import of raw materials as well as an article on the uses of nitrocellulose in peace and war. Short biographical notices of Solvay and Nobel are included, and some information about the activities of the firm.

## MISCELLANEOUS.

**Russian Equivalent Tables.**—In view of the increasing importance of trade with Russia the issue of information regarding the somewhat complicated Russian weights and measures, and especially of equivalent tables permitting of instant conversion of British weights, measures, and money into Russian, and *vice versa*, is of considerable interest to the trading community. The Central Translations Institute have compiled from official figures a set of tables covering all ordinary commercial requirements at the price of one shilling, and our readers will doubtless be glad to know of this useful and timely publication.

**Swansea Technical College.**—At a special meeting in connection with the Swansea Technical College, held last week, Mr. B. D. Skirrow, H.M.I. of Swansea, stated that a chemical and metallurgical department had been started in the borough in 1898 occupying two buildings. The work had gone on increasingly, and the accommodation now provided in the college was quite inadequate. Prof. Turner, of Birmingham, who was present, said he understood Swansea seriously contemplated making a step forward in connection with the educational facilities of the town. The essential point was that Swansea for centuries had been a very important centre of metallurgical industries, and another point was that they were concerned largely with the crude metal trades, such as the production of copper and spelter. But even these trades had not advanced in this district as they had in other districts in this country during the last fifty years, and certainly they had not advanced as they had in other parts of the world. He pointed out that wages were better and work more regular in the finishing trades, and if they were to have workmen to engage in these finishing trades it was necessary that they should provide instruction to make skilled workmen. There was no doubt as to the inadequacy of the technical school from a chemical and metallurgical point of view. They had made practically no advance for many years, while Sheffield, Birmingham, Glasgow, Manchester, and London had been establishing departments in this direction. With regard to the site they had selected for the new building close to the present college it was large enough for all they would require for many years to come. The cost of the new building will be roughly £24,000.

## NOTES AND QUERIES.

\* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Cellulose Acetate.**—In answer to your correspondent's enquiry, I can offer either variety of cellulose acetate of English manufacture for prompt and forward delivery.—LEONARD J. ALLCHIN, 27, Clarence Place, Gravesend, Kent.

## MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Royal Society of Arts, 8. (Cantor Lecture). "House Building," by M. H. Baillie Scott.

TUESDAY, 23rd.—Royal Institution, 3. "The Belief in Immortality among the Polynesians," by Prof. Sir J. G. Fraser.

WEDNESDAY, 24th.—Royal Society of Arts, 5.30. "The Work of the War Refugees' Committee," by Lady Lugard.

THURSDAY, 25th.—Royal Institution, 3. "The Ground beneath London" by Dr. Aubrey Strahan.

Royal Society. "Forms of Growth resembling Living Organisms and their Products slowly Deposited from Meta-stable Solutions of Inorganic Colloids," by B. Moore and W. G. Evans. "Production of Growths or Deposits in Meta-stable Inorganic Hydrosols," by B. Moore. "Chemistry of Coat Colour in Animals and of Dominant and Recessive Whiteness," by H. Onslow.

FRIDAY, 26th.—Royal Institution, 9. "Experiments in Slow Cathode Rays," by Prof. Sir J. J. Thomson, O.M.

SATURDAY, 27th.—Royal Institution, 3. "Recent Researches on Atoms and Ions," by Sir J. J. Thomson, O.M.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2887.

## THE NITROGEN OF PROCESSED FERTILISERS.\*

By ELBERT C. LATHROP,  
Scientist in Soil Fertility Investigations.

### INTRODUCTION.

ORGANIC compounds have lately taken on a deeper significance in their relation to the complex problems of the soil and of crop production, for not only do they affect the physical conditions and chemical reactions of the soil but they also have been shown to be directly connected with fertility or infertility, some of them being essentially beneficial to the growth of plants, while others are distinctly harmful. Of the organic compounds thus far isolated from soils, a large number contain nitrogen, and of these nitrogenous substances some have been found rather widely distributed in soils varying as to location, climate, methods of cropping, &c. These nitrogenous compounds occur either as plant constituents or arise from the decomposition of plant or animal protein, brought about by the various biological and biochemical agents in the soil. Not only compounds of this class found in soils but also many other protein decomposition products have been studied, both alone and in conjunction with the three fertiliser elements, in respect to their action on plant growth, and they have been shown in a number of cases to exert a beneficial influence; furthermore, these complex compounds are available for use by the plant without first being changed by chemical or biochemical means into ammonia and then to nitrates.

(NOTE.—“A Beneficial Organic Constituent of Soils: Creatinine,” by Oswald Schreiner, E. C. Shorey, M. X. Sullivan, and J. J. Skinner, *Bul.* 83, Bur. Soils., U.S. Dept. Agr., 1911. “Nitrogenous Soil Constituents and their Bearing on Soil Fertility,” by Oswald Schreiner and J. J. Skinner, *Bul.* 87, Bureau of Soils, U.S. Dept. Agr., 1912. This investigation is a contribution to the knowledge of the nature of the changes brought about in the manufacture of some of the processed fertilisers, and of the character and availability of such processed goods in mixed fertilisers when used in farm practice).

That these facts have an immense practical bearing on fertilisers and the fertiliser industry, both from the standpoint of the producer and of the consumer, is at once obvious. The old high-grade nitrogenous fertilisers, such as cottonseed meal, dried blood, fish scrap, &c., are being used more and more for feed purposes, and the time can not be far distant when their use as fertilisers will cease to be economic; thus a necessity for other and cheaper fertilisers of this type arises. Coupled with this is the desire of the chemist and the manufacturer to utilise in one way or another all waste products, whatsoever their nature, so that the number and kinds of nitrogenous materials which are used in the manufacture of fertilisers is on the increase. Described in the patent literature and found on the market are a large number of fertilisers which may be characterised as “processed,” that is, the crude materials, not in themselves permissible as fertilisers, are made to undergo some decided chemical change to render them suitable as plant nutrients. It has been found that the “availability” of the crude substances is nearly always greatly increased by such processing and that a much larger percentage of the nitrogen in the finished product is soluble in water, although the actual chemical changes produced seemed to have received little attention. The

chemical compounds in processed fertilisers which are here shown to have direct fertiliser significance have not been determined, other than to show that ammonia is formed during processing and that ammonia is more readily produced from the processed goods.

Since the wastes from which this type of fertiliser is made contain more or less protein, or protein-like substances, it seemed quite obvious that the finished fertilisers must contain more or less of the chemical compounds which would arise by such treatment from pure proteins in the laboratory. Since the action on plants of many of this class of compounds has been determined it is evident that the finding of such compounds in the fertilisers would throw much light on the question of the “availability” of the nitrogen in the fertiliser itself.

### BASE GOODS A TYPE OF PROCESSED FERTILISER.

For a chemical study of processed fertilisers a sample of “wet-mixed” or “base goods” fertiliser was chosen as a representative of this type of fertiliser material. The base goods was obtained directly from the factory for use in this investigation. This fertiliser is made by the treatment of various trade wastes and refuse, such as hair, garbage tankage, leather scraps, &c., with rock phosphate and the requisite amount of sulphuric acid. These materials are mixed together in a “den” and the resulting mass is allowed to stand for several days, until it is cool enough to be conveniently handled. In the course of the reaction the mass reaches a temperature approximating 100° C., and the identity of the original substances is almost or entirely lost. Under these conditions it is certain that more or less hydrolysis of the proteins in the crude materials takes place, with the formation of proteoses, peptones, polypeptides, or the simple amino acids, the kinds and number of products formed necessarily depending on the proportion of the different proteins in the original materials, on the amount and strength of the acid, the length of time of the reaction, and the temperature reached during the treatment.

Hartwell and Pember (*Journ. Ind. Eng. Chem.*, 1912, iv., 411) have recently made a study of base goods in order to determine the availability of the nitrogen contained in it as compared with that of the high-grade nitrogenous fertilisers. The product which they used was made from hair tankage, garbage tankage, and roasted leather, together with rock phosphate and sulphuric acid. From their report the following figures for the analysis of the crude materials used in producing the fertiliser and of the finished product are taken:—

TABLE I.—Total Nitrogen in Crude Materials and Finished Product. (Hartwell and Pember).

	Nitrogen, per cent.
Hair tankage .. .. .	6.28
Roasted leather .. .. .	6.49
Garbage tankage .. .. .	2.87
Base goods, including the above .. ..	1.68
Water soluble nitrogen in base goods ..	1.28
Water insoluble nitrogen in base goods ..	0.40

TABLE II.—Percentage of the Total Nitrogen present in different forms. (Hartwell and Pember).

	Before putting into the den.	After removing from the den.
In ammonia .. .. .	6.5	14.3
In water soluble organic matter ..	7.8	57.7
In water insoluble organic matter ..	85.7	28.0

The experimental work of the present investigation was along two separate lines: (1) Analytical, involving total nitrogen determinations and the separate estimation of the various forms in which nitrogen may occur; (2) a determination of the definite chemical compounds present in the fertiliser by suitable methods of isolation and identification.

\* Bulletin No. 158, United States Department of Agriculture, Bureau of Soils.

## THE CHEMICAL EXAMINATION OF BASE GOODS.

*Total Nitrogen and Ammonia.*

**Total Nitrogen.**—The total in the base goods was determined by the Kjeldahl-Gunning-Arnold method and was found to be 1.61 per cent (*Circular* 108, p. 15, U.S. Dept. Agriculture, Bureau of Chemistry, 1912; T. C. Trescott, *Journ. Ind. Eng. Chem.*, 1913, v., 914).

**Ammonia.**—Considerable difficulty was experienced in obtaining concordant results in the determination of the nitrogen in the form of ammonium salts. Boiling weighed amounts of the base goods with water and magnesium hydroxide, according to the official method (*Bul.* 107, 9, Revised, Bureau of Chem., U.S. Dept. Agr.), for the determination of ammonia in fertilisers, did not give duplicate results sufficiently close for the purpose of this research. Owing to the acidity of the sample, it was impractical to use barium carbonate, but litharge was used with varying results. Finally, the determination was made by using the vacuum distillation method, which gave concordant results. This method, which gives only the nitrogen found as ammonia or as ammonium salts, is used for the determination of amide nitrogen in the products of acid hydrolysis of proteins. A weighed quantity of the fertiliser was placed in a Claisen flask connected up with a cooled receiver of 1 litre capacity and a small guard flask of 200 cc. capacity. Both flasks contained 0.1 N sulphuric acid. To the fertiliser was added 100 cc. of neutral 95 per cent alcohol and 100 cc. of distilled water, together with enough 10 per cent suspension of calcium hydroxide to make the mixture decidedly alkaline in reaction. The ammonia was then distilled under a pressure of from 10 to 12 mm., the temperature of the bath not exceeding 40° C. In the table which follows are given the results obtained by the three methods here used for the determination of ammonia.

TABLE III.—*Nitrogen in the form of Ammonia or Ammonium Salts.*

Method.	Expressed in per cent of base goods.		Expressed in per cent of total nitrogen in base goods.	
Magnesium hydroxide distillation ..	0.380	0.389	23.60	24.16
Lead oxide distillation ..	0.394	0.420	24.47	26.09
Vacuum distillation ..	0.374	0.374	23.23	23.23

An examination of these results shows that by boiling with magnesia or litharge, somewhat more nitrogen is found as ammonia than really exists in this form in the base goods. It is therefore probable that there are in the base goods nitrogenous compounds which are broken down into ammonia by the action of these alkaline reagents at a temperature of 100° C. The use of magnesia at boiling temperature for the purpose of determining the amount of ammonia split off by acid hydrolysis from certain proteins which contained cystine, was found to give unreliable results (Embsen, quoted by Gumbel, "Hofmeister's Beiträge," 1904, v., 297; Hart, *Zeit. Phys. Chem.*, 1901, xxxiii., 354; Folin, *Ibid.*, 1903, xxxix., 476; Denis, *Journ. Biol. Chem.*, 1910, viii., 427). The reason for this was found to be that magnesia under such conditions changes a part of the amino nitrogen of cystine into ammonia. In this laboratory it was also found that by boiling cystine with lead oxide one of the amino nitrogen groups of this compound was split off almost quantitatively, with the concurrent splitting off of hydrogen sulphide. Furthermore, it has been shown that if the amide nitrogen from protein hydrolysis is determined by distillation with a weak alkali, such as calcium hydroxide, at a temperature not to exceed 40° to 42° C. in the bath and at a pressure of from 10 to 12 mm., no decomposition of cystine takes place (Gumbel, "Hofmeister's Beiträge," 1904, v., 297).

In the manufacture of base goods the hair which is used contains proteins which on acid hydrolysis yield a high percentage of cystine. This fact, together with the analytical results just discussed, suggest rather strongly

that there is present in the base goods more or less cystine, although this evidence cannot be considered conclusive, since it is possible that in such a heterogeneous mixture there may be present other nitrogenous compounds which would be decomposed by magnesia or litharge with the liberation of ammonia.

*Nitrogen Partition.*

For the purpose of determining the different forms of nitrogen present in the base goods the method of Van Slyke (*Journ. Biol. Chem.*, 1911, x., 15) was followed in its essential details, except that the determination of cystine was not made. The method for the determination of this compound, according to the procedure used by Van Slyke, depends not upon a nitrogen determination but upon the determination of the amount of sulphur in the compounds precipitated by phosphotungstic acid. This determination when made on the hydrolytic products of acid digestion of pure protein may give quite satisfactory results, but the raw materials from which base goods are made contain many organic compounds other than proteins or protein decomposition products, and this is of course particularly true in the case of garbage tannage. It is well known that many plant and animal substances contain sulphur in a variety of linkages, and garbage tannage no doubt contains sulphur in other forms than that of cystine. The hair and leather used have both undergone some decomposition before the acid treatment, and it is not impossible that the cystine originally present in the proteins may have been changed into sulphur compounds of a different chemical nature. No doubt some sulphur compounds other than cystine are precipitated by phosphotungstic acid, so that a determination of cystine depending on the sulphur content of the phosphotungstic acid precipitate would be of uncertain value in dealing with material of unknown origin and of such a heterogeneous character as fertiliser goods.

It should also be stated that although the results from the Van Slyke analysis are expressed in the usual way, arginine N, histidine N, &c., that is not intended to convey the impression that these fractions contain pure arginine, histidine, &c., since, as will be shown later, other compounds are included under these analytical terms. However, the nitrogen so expressed is that which is contained in compounds which give the various reactions upon which the Van Slyke method depends.

Two 20-grm. samples of base goods were extracted for analysis. The first sample was extracted with boiling water until the extract ceased to give an acid reaction. The second sample was boiled for twenty-four hours with hydrochloric acid, sp. gr. 1.115, the resulting solution was filtered by suction, and the insoluble residue washed with hot water until the washings ran free from chlorides. The two extracts were then concentrated to the consistency of a syrup *in vacuo* to expel the free volatile acid, and each was finally made up to a volume of 250 cc.

**Total Nitrogen.**—Total nitrogen in solution was determined by subjecting 50 cc. of the solution to Kjeldahl analysis. The water extract contained 1.372 per cent and the hydrochloric acid extract 1.435 per cent of the base goods.

**Amide Nitrogen.**—Amide nitrogen was determined by distilling *in vacuo* the remaining 200 cc. of solution, to which were added 100 cc. of 95 per cent alcohol and 20 cc. of a 10 per cent suspension of calcium hydroxide, as described under the determination of ammonia. The water extract contained 0.374 per cent and the hydrochloric acid extract 0.882 per cent.

**Humin Nitrogen.**—The residue from the amide nitrogen determination was used for the determination of humin nitrogen. The precipitate, formed by the addition of calcium hydroxide, was filtered off and washed with distilled water in the same manner in which Van Slyke directs that the phosphotungstic acid precipitate be washed. The washing was continued until no reaction for chlorides or alkalinity was obtained. The nitrogen re-



maining in the precipitate and in the filter-paper was then determined by Kjeldahl analysis. The humin nitrogen was 0.031 per cent for the water extract and 0.074 per cent for the hydrochloric acid extract.

**Diamino Acid Nitrogen.**—The combined filtrate and washings from the humin precipitate were neutralised with hydrochloric acid, concentrated *in vacuo* to a volume of about 100 cc., and then transferred to a 300 cc. Erlenmeyer flask. To this solution were added 18 cc. of concentrated hydrochloric acid together with 15 grms. of purified phosphotungstic acid (Winterstein, *Zeit. Phys. Chem.*, 1901, xxxiv., 153) and the whole diluted with water to a volume of 200 cc. The flask was placed on a steam-bath and heated until the phosphotungstates were almost re-dissolved, when it was set aside for forty-eight hours in order to allow them to re-crystallise and fully precipitate. The precipitate was then filtered, washed, and dissolved in 45 per cent sodium hydroxide as described by Van Slyke. The phosphotungstic acid was precipitated with barium chloride and filtered off. The filtrate and washings from this precipitate were concentrated *in vacuo* and made up to a volume of 200 cc.

**Arginine Nitrogen.**—Arginine nitrogen was determined in 100 cc. of this solution by boiling with 12.5 grms. of solid potassium hydroxide for six hours and collecting the ammonia formed in 0.1 N sulphuric acid. Under these conditions one-half of the nitrogen in the arginine and 18 per cent of the nitrogen of cystine is split off as ammonia.

**Total Nitrogen in the Diamino Acid Solution.**—Total nitrogen in the diamino acid solution was found by subjecting the solution remaining after the arginine determination to Kjeldahl analysis and adding to the ammonia so obtained the amount obtained from the arginine nitrogen determination.

**Amino Nitrogen.**—Amino nitrogen was determined by means of the Van Slyke apparatus. (For the description of this apparatus and the details of the procedure employed, see Van Slyke, *Journ. Biol. Chem.*, 1912, xii., 275).

From these three figures the nitrogen was calculated as arginine N, histidine N, and lysine N according to the two formulæ—

1. Histidine N =  $1.667 \text{ non-amino N} - 1.125 \text{ arginine N}$ ;
2. Lysine N =  $\text{total N} - (\text{arginine N} + \text{histidine N})$ .

The results obtained were as follows:—For the water extract arginine 0.111 per cent, histidine nitrogen 0.117 per cent, and lysine nitrogen 0.081 per cent; for the hydrochloric acid extract they were 0.104, 0.070, and 0.117 per cent respectively.

**Total Nitrogen of the Monoamino Acids.**—To the combined filtrate and washings from the phosphotungstic acid precipitate 45 per cent caustic soda was added until the solution became turbid by the precipitation of lime; acetic acid was then added until the solution cleared. This solution was placed in a 500 cc. flask and made up to the mark. Total nitrogen was estimated in 100 cc. portions, using the Kjeldahl method.

**Amino Nitrogen.**—Amino nitrogen in the form of monoamino acids was determined by use of the Van Slyke apparatus.

From the two figures obtained the amount of nitrogen present as *non amino nitrogen* in monoamino acids was found by difference. The amino nitrogen in the form of monoamino acids in the water extract was 0.543 per cent and in the hydrochloric acid extract 0.546 per cent. The non-amino nitrogen in the monoamino acid fraction of the water extract was 0.114 per cent and in the hydrochloric acid extract it was 0.133 per cent.

Van Slyke has shown that certain corrections must be applied in the method, owing to the fact that the phosphotungstates of the diamino acids are slightly soluble, and these corrections have been applied just as though the fractions contained only the hydrolysis products of pure proteins. In Table V the combined results of the analyses are given.

The above analytical procedure, which separates the nitrogen into different groups, gives results that can only be rigidly interpreted when the products of the acid hydrolysis are known. The results of the analysis of base goods by this method can only be clearly understood when further facts regarding the compounds, in which the nitrogen is contained, are discovered. A description of the methods used in isolating and identifying certain of these compounds follows.

(To be continued).

## THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.\*

By O. L. BARNEBEY.

(Concluded from p. 141).

### Theoretical.

A NUMBER of explanations have been offered to explain the function of manganese salts in the iron titration with permanganate. Volhard (35) explains the action by assuming the formation of tetravalent manganese ( $\text{MnO}_2$ ), which then oxidises the ferrous iron more rapidly than it does hydrochloric acid. Wagner (49) assumes the intermediate formation of  $\text{FeCl}_2 \cdot 2\text{HCl}$  in the absence of manganese sulphate, which oxidises very rapidly, consuming more permanganate than is required for ferrous iron. Zimmerman (5) suggested that, in absence of manganese salts, the iron is converted into a peroxide which is unstable, and at once forms ferric iron and oxygen, the latter acting upon the hydrochloric acid. Manchot (60) explains the action by assuming the formation of "primary oxides" of the peroxide nature, but which tend to revert immediately to oxides of a lower state of oxidation. According to this theory oxidation caused by oxygen forms  $\text{FeO}_2$ ; by permanganate, chromic acid, hydrogen peroxide, &c.,  $\text{Fe}_2\text{O}_5$ , and with hypochlorous acid,  $\text{FeO}_3$ . Hence the reaction is assumed to go somewhat as follows:—Oxygen forms  $\text{FeO}_2$ ,  $\text{FeO}_2$  oxidises  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_7$  oxidises  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$  with the formation of  $\text{MnO}_2$ , the  $\text{MnO}_2$  then oxidises  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ . If the hydrochloric acid is too strong then the  $\text{Fe}_2\text{O}_3$  reacts with the HCl liberating chlorine. Birch (23) suggests the formation of  $\text{MnCl}_3$ , which in turn has a greater tendency to oxidise ferrous iron than hydrochloric acid. This last assumption seems to warrant a more general consideration than has been accorded to it. While hydrated manganese peroxide can be assumed to exist for a brief space of time in the hydrosol condition, yet  $\text{MnCl}_3$  has not been definitely proven to exist in such a solution. The same argument can be applied to a theory requiring assumptions of  $\text{FeO}_2$ ,  $\text{FeO}_3$ , and  $\text{Fe}_2\text{O}_5$ .

Pickering (36) has shown that when manganese dioxide is treated with hydrochloric acid manganese sesquichloride results. A number of other authors have studied the formation of trivalent manganese in solution, especially sulphuric, hydrochloric, hydrofluoric, and phosphoric acids, and alkaline cyanides, a number of trivalent salts and double salts being separated from such solutions. (See references under heading, "Theoretical"). Meyer (59) has recently pointed out the definiteness of these compounds in acid solutions, and also shows that even when potassium manganicyanide hydrolyses a trivalent manganese hydroxide results. Schilow (61) has explained the reaction of potassium permanganate with oxalic acid on the basis of the intermediate formation of trivalent manganese. Skrabal (16) outlines the oxalic acid oxidation, and also that of manganese in alkaline solution through the formation of manganese of the valence of three. Muller and

\* From the *Journal of the American Chemical Society*, xxxvi., No. 7.

Koppe (6.) point out an error in the titration of manganese by the permanganate method in the presence of fluorides due to the formation of  $\text{MnF}_3$  and  $2\text{KF} \cdot \text{MnF}_3$ .

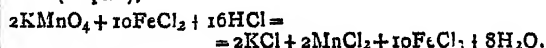
When potassium permanganate is added to a manganese solution containing an excess of phosphoric acid a deep red to violet coloration is obtained; when added to a manganese solution with hydrochloric acid in excess a greenish brown to black solution results; when added to a manganese sulphate solution in the presence of an excess of sulphuric acid a deep red to purple colour is imparted to the solution. Solutions of this nature contain manganese sesquisalts. The possibility of tetravalent manganese being present at ordinary temperatures in significant quantity is apparently quite remote. While very small amounts may be present, practically all attempts to prepare salts in which manganese has the valence of four from such solutions have been negative—only trivalent salts crystallising from them. More confirmation seems to be necessary to establish the existence of tetravalent manganese in even small quantity in these acid solutions. However, if tetravalent manganese is present the mechanism of the reaction to be later described would partially be explained through medium of its formation, and the fundamental idea of prevention of the chlorine or hypochlorous acid formation remains the same.

In the presence of hydrochloric acid these manganese sesquisalt solutions have a tendency to preserve the oxidation value of the solution; in other words, prevent the rapid loss of chlorine or hypochlorous acid. This preservation can be shown in open beakers qualitatively in a striking manner by adding 10 cc. of 0.1 N permanganate to 50 cc. of 50 per cent manganese sulphate solution containing 10 cc. of concentrated hydrochloric acid, and to 50 cc. of water containing a like volume of the acid. In a moderately short time the second solution loses its chlorine in sufficient quantity to become much lighter in colour than the first, and in a few hours becomes completely colourless, but the solution containing the manganese maintains its colour for weeks. Two such solutions in duplicate were prepared August 15 at 9 A.M. Both gave a decided odour of chlorine. At 9 A.M. the following day the two solutions containing the manganese were still brownish black, but the two without the manganese were practically colourless. On September 5 the two containing the manganese were light brown, and on November 18 the colour still persisted, and a few cc. of the solution gave an evolution of iodine when potassium iodide was added. Water was added from time to time to replace what was lost by evaporation.

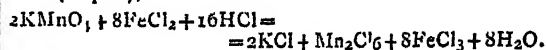
In the titration of iron in hydrochloric acid solution it has been shown that manganous and cerous salts used in moderate amounts, and certain acid phosphate and sodium sulphate solutions, prevent the loss of chlorine or hypochlorous acid during titration, and enable correct results to be obtained in the presence of hydrochloric acid. Evidently the reactions of these preventives involve two different types of effects. One effect is transposition from chloride to salts of another acid by the mass action of the preventive. The other effect is the formation of an intermediate compound or compounds which have the capacity to oxidise the ferrous iron, preventing the loss of chlorine. In a preventive one or the other effect may be in predominance. In the case of sodium sulphate the first effect is the larger, but some manganese is in solution due to the products of reaction, and must exert some influence. In the case of manganese sulphate and sulphuric acid we have both effects with the second the larger, a mixture of sesquichloride and sulphate being produced as intermediate products. When manganese sulphate, phosphoric acid, and sulphuric acid are employed, the opportunity for a larger number of sesquisalts to be formed is increased correspondingly with the same effect as that produced by the more simple mixtures. With manganese chloride as preventive, the intermediate sesquimanganese chloride gives the only effect toward preven-

tion. In these cases the reactions may be represented by the following equations.—

1. (In part),—



2. (In part),—



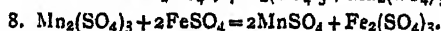
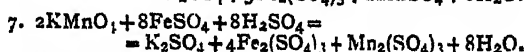
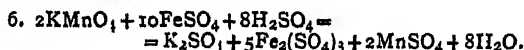
3.  $\text{Mn}_2\text{Cl}_6 \rightleftharpoons 2\text{MnCl}_2 + \text{Cl}_2$ .

4.  $\text{Cl}_2 + \text{FeCl}_2 \rightarrow \text{FeCl}_3$  (slow).

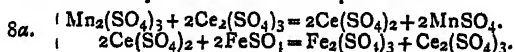
5.  $\text{Mn}_2\text{Cl}_6 + 2\text{FeCl}_2 = 2\text{FeCl}_3 + 2\text{MnCl}_2$  (more rapid than 4).

The permanganate oxidises a considerable portion of the iron according to Equation (1). However, some  $\text{Mn}_2\text{Cl}_6$  is formed, Equation (2). This sesquichloride is unstable, and has a tendency to decompose, liberating chlorine (3). The smaller the amount of manganese present the more rapid is this decomposition; the larger the amount of manganese the greater the tendency to retard the evolution of chlorine. The chlorine oxidises the ferrous iron slowly (4). Manganese sesquichloride oxidises ferrous iron much more rapidly than does free chlorine (5). Hence, if the reaction represented by Equation 3 is forced to proceed toward the left by the addition of manganese chloride, preserving the initial character of the  $\text{Mn}_2\text{Cl}_6$ , the loss of oxidation effect due to chlorine evolution may be prevented, and the final reaction follows the theoretical value (1).

When the Reinhardt-Zimmerman, Mixer-Du Bois, or other solution of similar nature is employed the first list of reactions takes place partially, but the larger portion of the reaction occurs through the medium of some other acid than hydrochloric—usually phosphoric or sulphuric. In case of sulphuric acid this portion of the reaction can be thus illustrated:—



When cerium sulphate is used for the prevention:—



When phosphoric acid is used the reaction probably occurs through the medium of acid phosphates, involving corresponding change of valences.

#### Analysis of Iron Ores with various Preventives.

A number of iron ores were analysed using the solutions heretofore described:—(a) Sodium sulphate; (b) potassium phosphate and phosphoric acid; (c) sodium phosphate and phosphoric acid; (d) manganese sulphate and sulphuric acid; (e) manganese sulphate, phosphoric and sulphuric acids; (f) cerium sulphate and sulphuric acid. The sample in each case was decomposed by heating with about 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and sufficient stannous chloride solution to almost reduce all of the iron. After complete solution of the iron the reduction was finished by adding stannous chloride drop by drop to the hot solution until one drop just made it colourless, then one drop was added in excess. After dilution to about 500 cc., 10 cc. of mercuric chloride was added all at once with vigorous stirring. One of the preventives above noted was added, and the iron titrated. The results from four representative ores are listed in Table XV.

#### Discussion of the End-point.

The end-point in the titration of iron is more stable in sulphuric and phosphoric than in hydrochloric acid solutions. In the last named the pink tinge imparted to the solution, showing a slight excess of permanganate, is more

fleeing. While the addition of the preventives enumerated allows a correct iron analysis to be made within the range of error expected of such an analysis, nevertheless, when the permanganate is added in excess, as at the end of the titration, a fading effect becomes more or less marked. On this account an analyst accustomed to the iron titration in hydrochloric acid solution calls the first slight tinge of colour permeating the entire solution the end-point. The tinge is much lighter than the tint in sulphuric or phosphoric acid solutions free from hydrochloric acid. This difference is at least partially due to the difference in colour of the sesquichloride and sulphate and phosphate solutions. This variance in stability may account for some of the conflicting analyses heretofore published.

TABLE XV.  
Series XV.—Analyses of Iron Ores with various Preventives.

Ore No.	Sample No.	Weight of sample. Grm.	Preventive.		Fe found. Per cent.
			Kind	Volume. Cc.	
20	1	0.5000	a	200	65.91
20	1	0.5000	b	30	65.96
20	1	0.5000	c	30	65.96
20	1	0.5000	d	15	65.91
20	2	0.5000	d	15	66.07
20	1	0.5000	e	15	66.07
20	2	0.5000	e	15	65.96
20	1	0.5000	f	25	65.96
20	2	0.5000	f	25	65.98
21	1	0.4000	a	200	57.44
21	1	0.4000	b	25	57.44
21	2	0.4000	b	25	57.50
21	1	0.4000	e	25	57.41
21	1	0.4000	f	30	57.52
26	1	0.7000	a	200	35.60
26	1	0.7000	b	30	35.71
26	1	0.7000	c	30	35.64
26	1	0.7000	d	20	35.64
26	1	0.7000	e	20	35.74
26	1	0.7000	f	30	36.68
43	1	0.8000	a	200	33.80
43	1	0.8000	b	25	33.77
43	2	0.8000	b	25	33.84
43	3	0.8000	b	25	33.84
43	1	0.8000	c	30	33.81
43	2	0.8000	c	30	33.86
43	1	0.8000	d	20	33.33
43	2	0.8000	d	20	33.94
43	1	0.8000	e	20	33.85
43	2	0.8000	e	20	33.79
43	1	0.8000	f	20	33.87

The end-point in the titration of ferrous to ferric sulphate in the presence of sulphuric acid and in the absence of hydrochloric acid is almost as clean cut in the ordinary iron analysis as in phosphoric acid solution. Analysts recognise this fact in the standardisation of permanganate against ferrous ammonium sulphate and metallic iron, in which case the end-point is much more clear than in the regular titration of iron ores in the presence of suspended calomel even when phosphoric acid is added. However, this much must be said, if phosphoric acid is added by an analyst to give what to his eye seems to be a clearer end-point in the analysis of the iron containing product, then the analyst who is having trouble with this colour change must, to be consistent, add phosphoric acid in standardisation if he standardises the permanganate against an iron containing standard.

One gram. of iron present as ferric sulphate with a little free sulphuric acid in a volume of 400 to 500 cc. gives a recognisable colour change with 0.04 cc. of tenth normal permanganate. Of course this coloration is not red or pink, but it is a distinct change of colour. Twice the above amount of permanganate gives a very decided coloration. These observations were naturally made against a white

background. A moderate amount of experience with the iron titration allows a very sharp end-point with moderate amounts of iron (up to about 0.6 gm. metal) without the presence of a decolorising influence; however, when a large amount of iron (over 0.6 gm. metal) is to be titrated the addition of phosphoric acid is to be recommended, although, with care, larger amounts can be titrated with accuracy. With smaller amounts the addition of the phosphoric acid is optional with the analyst. Since ordinarily the amount of iron present in the solution being titrated is about 0.3 gm. or less it seems to the author that the use of a decoloriser is unnecessary.

#### Summary.

1. Correct results are obtained with a mixture of manganese sulphate, sulphuric acid, and phosphoric acid for the prevention of the action of hydrochloric acid on permanganate. The use of phosphoric acid in the presence of considerable sulphuric acid in a volume of 400 to 600 cc. has very little tendency to decolorise the solution, inasmuch as the sulphate solution is practically colourless, except when titrating large amounts of iron. Hence, the elimination or use of phosphoric acid with the sulphuric acid and manganese sulphate is largely a matter of individual preference rather than a fundamental difference in the analysis.

2. When a titration runs too high, the amount of variance from the true value is dependent on the amount of mercurous chloride present in suspension as well as on the concentration of hydrochloric acid.

3. Certain neutral sulphates and acid phosphate mixtures react with hydrochloric acid, and prevent the latter from causing high results in the iron titration. The acid phosphate solutions are especially serviceable.

4. Cerous sulphate shows the same deportment in the titrating solution as manganese sulphate.

5. Sodium sulphate, acid phosphate mixtures, manganese sulphate with sulphuric acid, manganese sulphate with phosphoric acid, or with both acids, can be applied to iron ore analyses. The use of cerous sulphate, while effective, is as yet prohibited on account of the present cost of the chemical.

6. The prevention of the various reagents studied may be considered of two types:—(1) Conversion to salts of other acids than hydrochloric by the mass action of the preventer, and (2) the formation of intermediate compounds, which in turn oxidise ferrous to ferric iron with or without the first type being effective at the same time.

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See also the references under the title "Experimental."

## THE SEPARATION OF THE ILLUMINANTS IN MIXED COAL AND WATER GAS.

B. G. A. BURRELL and I. W. ROBERTSON

## Introduction.

IN this paper are shown experiments made by the Bureau of Mines that resulted in separating the illuminants in the artificial gas of Pittsburgh. This gas is made by mixing one part of carburetted water gas with three parts of coal gas. The separation was made by fractionally distilling the gas in a vacuum at low temperatures, and follows the method detailed by the Bureau in separating natural gases (G. A. Burrell and F. M. Seibert, "Gas Analysis by Fractional Distillation at Low Temperatures," *Journ. Amer. Chem. Soc.*, xxxvi., No. 7, July, 1914, 1538-1548).

## TABLE I.

## PART I.—Distillates

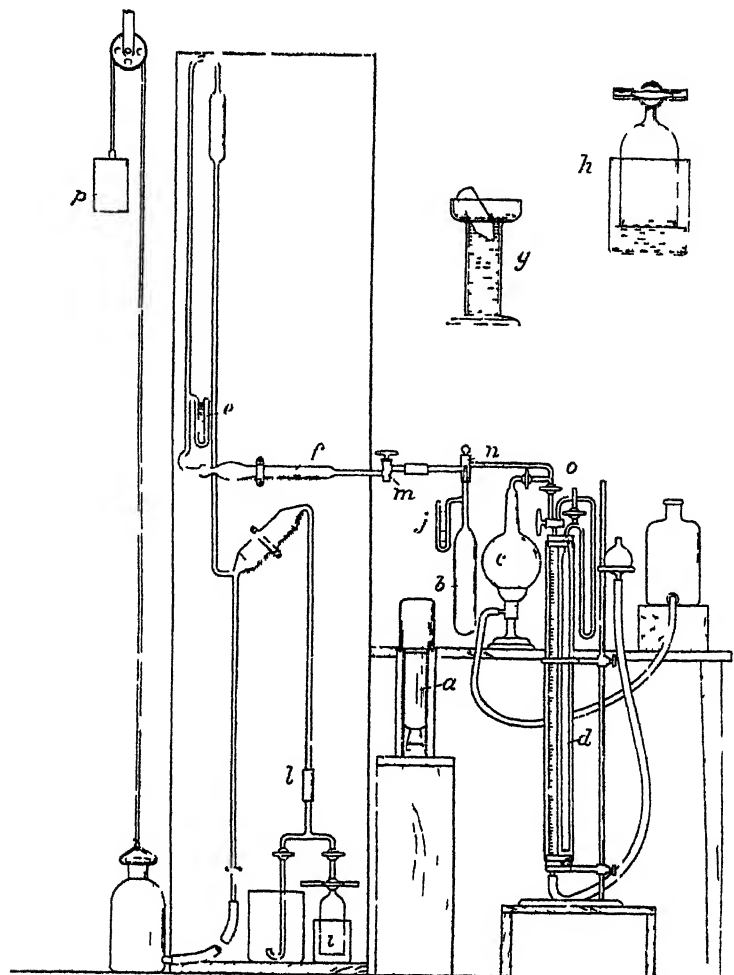
	Boiling point (°C)
Temperature of Liquid Air.	
Methane, CH <sub>4</sub> .. .. .	-160
Nitrogen, N <sub>2</sub> .. .. .	-195
Oxygen, O <sub>2</sub> .. .. .	-183
Carbon monoxide, CO .. .. .	-193
Hydrogen, H <sub>2</sub> .. .. .	-253
-155° C. to -145° C.	
Ethylene, C <sub>2</sub> H <sub>4</sub> .. .. .	-103
Ethane, C <sub>2</sub> H <sub>6</sub> .. .. .	-93
-130° C. to -120° C.	
Propane, C <sub>3</sub> H <sub>8</sub> .. .. .	-45
Propylene, C <sub>3</sub> H <sub>6</sub> .. .. .	-51
-78° C.	
N-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	1
Iso-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	-10
Iso butylene, C <sub>4</sub> H <sub>8</sub> .. .. .	-4

## PART II.—Residues.

Temperature of Liquid Air.	
Ethane, C <sub>2</sub> H <sub>6</sub> .. .. .	-93
Propane, C <sub>3</sub> H <sub>8</sub> .. .. .	-45
N-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	1
Iso-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	-10
Ethylene, C <sub>2</sub> H <sub>4</sub> .. .. .	-103
Propylene, C <sub>3</sub> H <sub>6</sub> .. .. .	-51
Iso butylene, C <sub>4</sub> H <sub>8</sub> .. .. .	-4 (a)
Benzene, C <sub>6</sub> H <sub>6</sub> .. .. .	80
-155° C. to -145° C.	
Propane, C <sub>3</sub> H <sub>8</sub> .. .. .	-45
N-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	1
Iso-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	-10
Propylene, C <sub>3</sub> H <sub>6</sub> .. .. .	-51
Iso-butylene, C <sub>4</sub> H <sub>8</sub> .. .. .	-4
Benzene, C <sub>6</sub> H <sub>6</sub> .. .. .	80
-130° C. to -120° C.	
N-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	1
Iso-butane, C <sub>4</sub> H <sub>10</sub> .. .. .	-10
Iso-butylene, C <sub>4</sub> H <sub>8</sub> .. .. .	-4
Benzene, C <sub>6</sub> H <sub>6</sub> .. .. .	80
-78° C.	
Benzene, C <sub>6</sub> H <sub>6</sub> .. .. .	80

(a) The boiling-point of N-butylene could not be found in the literature. The N-butylene was not separated from the iso-butylene. Neither was the N-butane separated from the isobutane.

\* Presented at the meeting of the American Gas Institute, October 23, 1911, New York City, with the permission of the Director of the U. S. Bureau of Mines.



APPARATUS FOR THE LIQUEFACTION & FRACTIONATION OF GASES

In both the natural gas work and coal gas work advantage was taken of the work on the subject by P. Lebeau and A. Damiens (*Comptes Rendus*, 1913, clvi, 325, 797), who separated mixtures of the paraffin hydrocarbons and coal gas by the same method. The Bureau, however, separated the paraffin hydrocarbons into single constituents, and found it necessary to refractionate distillates and residues in all cases to obtain pure gases. Lebeau and Damiens make no mention of this latter necessity, and separated the paraffins in pairs. Further there is shown in this paper a simple method for the determination of benzene in artificial gas. The principle of the procedure rests on the fact that the gases at different stages in the analysis are subjected to temperatures at which certain constituents can be removed by a mercury pump from certain others which have low vapour tensions at the temperatures selected. It was found impossible to make a clean separation in any case at one fractionation, hence distillates and residues were refractionated until the separation was as complete as was desired.

Table I. shows the constituents in artificial gas that can be separated at different temperatures. The first part shows the distillates that can be obtained at a particular temperature and the second part the residues—i.e., those gases that have appreciable vapour pressures at the temperatures given.

TABLE II.—Composition of the Artificial Gas of Pittsburgh as Analysed by Ordinary Methods.

(Analysis made September 1, 1914).

Constituents	Per cent.
Carbon dioxide, CO <sub>2</sub> .. .. .	2.61
Oxygen, O <sub>2</sub> .. .. .	0.81
Illuminants .. .. .	8.67
Carbon monoxide, CO .. .. .	13.34
Hydrogen, H <sub>2</sub> .. .. .	37.04
Methane, CH <sub>4</sub> .. .. .	30.96
Ethane, C <sub>2</sub> H <sub>6</sub> .. .. .	1.82
Nitrogen, N <sub>2</sub> .. .. .	4.72
Total .. .. .	100.00

In making the analysis (Table II.) the carbon dioxide was removed by the caustic-potash solution, the oxygen by alkaline pyrogallate solution, the illuminants by fuming sulphuric acid, the hydrogen by absorption in colloidal-palladium solution, the methane and ethane by slow combustion, and the nitrogen by difference (see G. A. Burrell and G. G. Oberfell, "The Absorption of Hydrogen by Colloidal-Palladium Solution," *Journ. Ind. Eng. Chem.*, vi., No. 8, November, 1914).

The above gas was next subjected to fractional distillation at various low temperatures in the apparatus shown



at Fig. 1 (apparatus for the liquefaction and fractionation of gases). At *a* is shown a Dewar flask to hold the refrigerant used in cooling the gases; *b* is the bulb in which the gases were cooled; *d* is a gas-analysis burette, and *c* another gas container for measuring the gases prior to cooling; *e* is a pressure gauge for registering pressures in the Töpler pump; *f* is a drying tube containing phosphorus pentoxide for removing the water vapour from the gases; *g*, *h*, and *i* are containers for trapping the gases over mercury as they were removed from the pump; *h* and *i* are provided with 3-way stopcocks. The particular advantage of containers such as are shown at *h* and *i* lies in the fact that they could be filled with mercury by forcing down on them with the stopcock open to the air, finally filling the capillary tubes with mercury. The gas from the pump could then be introduced into them by means of the goose-neck tube attached to *l*, leaving a mercury seal in the capillary tube all the time. *j* is a pressure gauge, which was of principal use in the benzene determination; *o*, *n*, and *m* are 3-way stopcocks. A counterpoise (*p*) attached to the mercury reservoir of the Töpler pump greatly facilitated the working of the pump.

#### First Series of Fractionations.

At Fig. 2 are shown the various steps in the main separation of the gas.

The original volume of sample (2048 cc.) was first freed of the carbon dioxide by passing it through caustic-potash solution; 53 cc. of carbon dioxide was removed, leaving 1995 cc. The latter quantity of gas was then cooled in the bulb *b* (Fig. 1) (about 300 cc. at a time), at the temperature of liquid air. After the introduction of each 300 cc. pumping was started, and as much of the gas removed as possible. There resulted a distillate (*a*) and a residue (*b*). The distillate (*a*) was fractionated at the temperature of liquid air, resulting in two more fractions (*c*) and (*d*); (*d*) was added to the residue (*b*) and the total again fractionated at the temperature of liquid air. The distillate (*f*) thus obtained was added to the distillate (*c*) and the total again fractionated at the temperature of liquid air. The residue thus obtained (10 cc.) was added to the residue (*e*) and the total again fractionated. There resulted a distillate (*e*) of 3 cc., which was added to the distillate (*i*), making a total of 1782 cc. This first series of fractionations shows the general procedure. At the temperature adopted, in this case the temperature of liquid air, the gases were repeatedly fractionated until no more distillate of consequence could be obtained; 3 cc., the final distillate obtained, is only about 0.15 per cent of the original quantity of gas (2048 cc.) taken for the experiment. The total distillate obtained at the temperature of liquid air was 1782 cc., and consisted of those gases that have an appreciable vapour tension at that temperature. This fraction consisted of 0.81 per cent of oxygen, 13.25 per cent of carbon monoxide, 37.33 per cent of hydrogen, 31.13 per cent of methane, and 4.23 per cent of nitrogen. It will be observed that the quantities of these constituents check very well with the quantities of the same constituents found in the original ordinary analysis of the coal gas. The residue of the first series of fractionations (191.6 cc.) should consist of those gases and vapours that do not have an appreciable vapour pressure at the temperature of liquid air: they are:— $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_2H_4$ ,  $C_3H_6$ ,  $C_4H_8$ , and  $C_6H_6$ . In other words, the so-called illuminants of coal gas, with the addition of ethane and probably propane.

#### Second Series of Fractionations.

The residue (*h*) (191.6 cc.) was next cooled at temperatures ranging from  $-155^{\circ}C.$  to  $-145^{\circ}C.$ , and as much gas removed as possible with the mercury pump. Distillates and residues were repeatedly fractionated until there was obtained 167.0 cc. of gas consisting of ethane and ethylene. This fraction was analysed in two ways, first by burning the entire fraction with oxygen, and (2)

by first removing the ethylene with fuming sulphuric acid and then burning the ethane in oxygen. The data covering these two methods of analysis is given in Table III.

TABLE III.—Analysis of Ethane and Ethylene.  
Analysis by Combustion.

	Cc.	Per cent.
Sample taken . . . . .	15.12	
Oxygen added . . . . .	94.42	
Total volume . . . . .	109.54	
Volume after burning . . . . .	78.00	
Contraction produced . . . . .	31.54	
Volume after KOH absorption . . . . .	48.27	
Carbon dioxide produced . . . . .	29.73	
Ethane . . . . .		23.90
Ethylene . . . . .		74.40

#### Analysis by Absorption and Combustion.

Sample taken . . . . .	34.18	
After absorption in fuming $H_2SO_4$ . . . . .	8.85	
Absorbed by fuming $H_2SO_4$ . . . . .	25.33	
Oxygen added . . . . .	76.28	
Total volume for combustion . . . . .	85.13	
Volume after burning . . . . .	64.95	
Contraction . . . . .	20.18	
Volume after KOH absorption . . . . .	49.02	
Carbon dioxide produced by burning . . . . .	15.93	
Ethane . . . . .		23.3
Ethylene . . . . .		74.1

It will be observed that the ethane and ethylene as found by the two methods of analysis check very well, showing that other gases were not present in the distillate in significant amounts. The percentages as found above were averaged and calculated to percentages of the original coal-gas.

#### Third Series of Fractionations.

After the removal of the ethane and ethylene there remained 24.4 cc. of gas, which was fractionated at temperatures ranging from  $-130^{\circ}C.$  to  $-120^{\circ}C.$  The distillate, 21.1 cc., was analysed by burning it in oxygen, and measuring the resulting contraction and carbon dioxide, and calculating to propane and propylene. This method does not isolate the gases, and hence does not show that other gases than these two were not present. In working on the separation of the paraffin hydrocarbons, however, the Bureau found that propane could be separated from ethane at temperatures between  $-130^{\circ}C.$  and  $-120^{\circ}C.$  Propylene has a boiling-point very close to propane, and the boiling-point of ethylene is not far different from that of ethane; hence, it is assumed that propylene and ethylene would respond to the same treatment as the propane and ethane.

(To be continued).

#### ON IRON CASTING.

By SERGIUS KERN, M.E., Petrograd.

In addition to my article in the CHEMICAL NEWS (cxii., 3), I want to state that the product obtained is in no case the so-called semi-steel, but close grained cast-iron, where the percentage of metallic iron is increased by the addition to the cupola charge of wrought iron or steel scrap up to no more than 15 per cent.

By acting so the percentage of free crystalline graphite in the iron is reduced to nearly nought, giving close grained iron castings, as this graphite is absorbed by the free iron introduced, and transformed into amorphous graphite.

I started always in the foundry I directed by test-melting of new brands of iron in crucibles, by mixing them, firstly, with 5 per cent of iron or steel scrap, next with 7.5 per cent, and so on. When good mechanical tensile tests were here obtained in the cupola charge, the iron or steel scrap was increased by 2.5 to 5 per cent in comparison with the same charge for crucible tests.

Once I had the following pig iron from South Russia:—

	Per cent.
Graphite .. .. .	2.20
Combined carbon ..	0.80
Silicon (average) ..	1.80
Manganese .. .. .	0.80
Phosphorus .. .. .	0.30
Sulphur .. .. .	0.07

It gave good results when melted alone with 5 per cent of steel scrap in the crucible; I added to the cupola charge an extra 2.5 per cent of steel scrap, and obtained very decent results:—10.5 to 11.5 tons per square inch in tensile strength, and 1.3 to 1.4 tons in the fracture tests.

## ON THE PREPARATION AND HYDROLYSIS OF ETHYL HYDRACRYLATE.\*

By W. A. DRUSHEL.

HYDRACRYLIC acid is a well-known substance, and has been prepared by several methods; its esters, however, have received but little attention. In Beilstein's "Handbuch" the ethyl ester alone is mentioned in connection with Klimenko's attempt to prepare paracrylic acid. Only three references are given to the ethyl ester in Richter's "Lexikon," and of these but one deals with the direct preparation of the ester. Apparently in no former investigation has hydracrylic ester been prepared by the esterification of hydracrylic acid, nor was the ester obtained in pure condition by any of the methods described in the literature. It seemed desirable, therefore, to prepare if possible hydracrylic ester by the direct esterification of hydracrylic acid in order to obtain the ester in pure condition for the purpose of determining its properties and supplying additional hydrolysis data for the series of esters studied in this laboratory.

### Preparation of the Ester.

(a) *Method of Klimenko* (*Journ. Russ. Chem. Soc.*, xxvi., 412).—Klimenko obtained what he called paracrylic acid by repeatedly evaporating hydracrylic acid with concentrated hydrochloric acid. He then heated 3 grms. of this acid with an excess of absolute alcohol at 150°, and obtained an ester which boiled at 185° to 190°, and which he believed to be ethyl hydracrylate. Ethyl hydracrylate, however, decomposes below 185° when heated at ordinary pressure. In attempting to repeat Klimenko's work the author was unable to prepare the so-called paracrylic acid by the method described. Baeyer (*Ber.*, xviii., 680) did not believe that Klimenko had succeeded in preparing paracrylic acid ( $C_3H_3O_2$ ), but rather that Klimenko's acid was an unsaturated dibasic acid of the formula  $C_6H_8O_4$ . If Baeyer's observation was correct Klimenko's ester could not have been hydracrylic ester.

(b) *Method of Curtius and Muller* (*Ber.*, xix., 850; xxxvii., 1276).—These investigators obtained impure ethyl hydracrylate by converting  $\beta$ -chloropropionic ester into  $\beta$ -aminopropionic ester hydrochloride and treating this with nitrous acid. The ester contained a little chloropropionic ester as an impurity, from which it could not be freed by fractionation. The crude ester which they obtained boiled at 80° to 84° at 12 mm. pressure or at 170° to

175° under ordinary pressure. The method is obviously not suitable for the preparation of the ester in sufficiently pure condition to study its properties and rate of hydrolysis.

(c) *Method of Blaise and Maire* (*Comptes Rendus*, cxlii., 215).—Blaise and Maire passed into glacial acetic acid at 0° the formaldehyde vapour obtained by the depolymerisation of trioxymethylene. The saturated acetic acid solution was then allowed to warm up slowly, resulting in a polymer of formaldehyde less complex than trioxymethylene. This polymer was condensed with bromacetic ester in the presence of zinc in a mixture of equal parts of absolute alcohol and ethyl acetate. They obtained a 40 per cent yield of ethyl hydracrylate whose boiling-point was given as 81° at 13 mm. pressure. It is to be observed that this boiling-point is about the same as that given for Curtius and Muller's admittedly impure ethyl hydracrylate.

(d) *Direct Esterification Method*.—In view of the instability of  $\beta$ -oxyacids on heating in the presence of mineral acids, and of the work of Bogojawlesky and Narbut (*Ber.*, xxxviii., 3344) on the use of anhydrous copper sulphate to facilitate esterification in the presence of acid catalysts, and the more recent work of Clemenson and Heitman (*Am. Chem. Journ.*, xl., 319) on the use of anhydrous copper sulphate in the esterification of certain oxyacids in the absence of any catalysing acid, it seemed reasonable to expect this procedure to be applicable for the preparation of pure ethyl hydracrylate. The work of preparing ethyl hydracrylate resolved itself into two parts—(1) the preparation of a sufficiently large amount of pure hydracrylic acid, and (2), the esterification of the acid.

1. *The Preparation of Hydracrylic Acid*.—Of the several methods described for the preparation of hydracrylic acid the method using glycerin as a starting-out material, with certain modifications, was found to be the most expedient for preparing the pure acid in considerable quantity. The modifications of former methods, which will be pointed out, resulted in increasing the yield and purity of the hydracrylic acid.

A kilo. of glycerin was mixed with a litre of water and oxidised in 200 cc. portions by fuming nitric acid in tubes about 20 mm. in internal diameter kept cold by running water, according to the procedure outlined by Mulder (*Ber.*, ix., 1902). After the oxidation was complete the liquid was concentrated in 400 cc. portions on the steam bath to remove any dissolved nitrous acid. On cooling some oxalic acid crystallised out. The filtrates from the several 400 cc. portions were combined and treated with a little more than enough calcium carbonate to precipitate out the dissolved oxalic acid as calcium oxalate, which was removed by filtration. The filtrate was diluted with water to 3 litres and heated to about 80°. The hot solution was neutralised with calcium carbonate, making use of mechanical stirring to facilitate the solution of the carbonate. The solution was allowed to stand over night for the main portion of the calcium glycerate to crystallise out. This first crop of calcium glycerate after washing with a little cold water was sufficiently pure for further use. The mother liquor, after making faintly acid to prevent darkening on heating, was concentrated on the steam bath and set aside to crystallise. After re-crystallising this second crop of calcium glycerate it was sufficiently pure, and was added to the first crop. The calcium glycerate so prepared was dissolved in hot water and treated with the theoretical amount of dissolved oxalic acid, the calcium oxalate was filtered off, and the filtrate concentrated on the steam bath to a specific gravity of 1.26, containing about 61 per cent. of glyceric acid. This is the most favourable concentration for converting glyceric acid into  $\beta$  iodopropionic acid by the action of phosphorus iodide.

For the preparation of  $\beta$ -iodopropionic acid a modification was introduced into the method of Wislicenus (*Ber.*, viii., 1207) and Erlenmeyer (*Ann. Chem. Pharm.*,

\* From the *American Journal of Science*, xxiv., p. 113

xcxi., 284), making use of solid yellow phosphorus instead of the carbon disulphide solution, whereby at last 90 per cent of the glyceric acid was converted into the iodopropionic acid. One hundred grms. of iodine were placed into a 750 cc. round-bottom flask and covered with 100 grms. of 61 per cent aqueous glyceric acid. Then 15 grms. of yellow phosphorus were added during the course of five minutes in pieces of about 1 grm. each, shaking the flask after the addition of each piece and cooling the flask by immersing it in a cold-water bath from time to time. The flask was next connected with a condenser tube to serve as a reflux condenser, and the mixture cautiously warmed on a water-bath to start the reaction of the phosphorus iodide with the glyceric acid. The reaction soon tends to become violent with the loss of large quantities of hydriodic acid. In order to prevent the loss of hydriodic acid as far as possible, the reaction was moderated by immersing the flask in cold water for a few minutes from time to time. After the first vigorous reaction was over the mixture was heated on the boiling water-bath for half an hour, poured into a beaker, covered with a watch-glass and set aside over night to crystallise. The crystals of pure  $\beta$ -iodopropionic acid were then filtered off with suction, washed with a little cold water, the filtrate boiled for an hour with a reflux condenser, and again set aside to allow more  $\beta$ -iodopropionic acid to crystallise out. The two crops of crystals were combined and re-crystallised from a little hot water, yielding white pearly plates of pure  $\beta$ -iodopropionic acid.

To prepare the sodium salt of hydracrylic acid a modification was introduced into the method of Wislicenus (*Ann. Chem. Pharm.*, clxvi., 10) for the conversion of  $\beta$ -iodopropionic acid into hydracrylic acid by the action of freshly prepared silver oxide. Sokolow (*Ibid.*, cl., 167) observed that when a water solution of  $\beta$ -iodopropionic acid is boiled with freshly prepared silver oxide the iodine is quickly fixed as silver iodide and that in solution are dihydracrylic acid,  $C_6H_{10}O_3$ , and an isomer of this acid besides the hydracrylic acid sought. Moldenhauer (*Ibid.*, clxvi., 10) also made the observation that considerable lactic acid is formed in this procedure. In order to avoid the formation of lactic acid and the acids identified by Sokolow, Wislicenus heated his solution below  $100^\circ$  while fixing the iodine by means of silver oxide. The silver which combined with the hydracrylic acid formed in the reaction he removed by means of hydrogen sulphide, neutralised the acids in solution with sodium carbonate, and evaporated to complete dryness. From the dry mixture of sodium salts Wislicenus extracted sodium hydracrylate with boiling 95 per cent alcohol, leaving in the residue the sodium salts of Sokolow's acids.

It was found preferable to modify this procedure by neutralising the  $\beta$ -iodopropionic acid with sodium carbonate, and then removing the iodine by acting upon a concentrated solution of sodium  $\beta$  iodopropionate with a slight excess of freshly prepared silver oxide at room temperature, making use of mechanical stirring during the process of replacing the iodine by the OH group. To remove completely the iodine from the sodium salt of 400 grms. of  $\beta$ -iodopropionic acid by this procedure required about two hours, but the resulting sodium hydracrylate was apparently free from the salts of the acids formed by the older methods and identified by Sokolow and others. After the complete fixation of the iodine as indicated by no further change in the colour of silver oxide when added to the solution, the precipitated silver iodide was filtered off and the filtrate evaporated to complete dryness over the steam bath. It is important that the sodium hydracrylate should be evaporated to complete dryness in order to be able to purify the salt by crystallisation from 95 per cent alcohol. The dried residue of sodium hydracrylate was dissolved in boiling 95 per cent alcohol and allowed to crystallise out on cooling. The residue of sodium salt was completely dissolved by the hot alcohol, indicating the absence of the sodium salts of Sokolow's acids. The

crystallised sodium hydracrylate was treated with a little less than the theoretical amount of dilute (1:3) sulphuric acid in the cold. The excess of water was then evaporated off on the steam bath, the hydracrylic acid was extracted from the residue of sodium sulphate with absolute alcohol, and the alcoholic solution of hydracrylic acid, free from sulphuric acid, was used in the esterification experiments to be described.

2. *The Esterification of Hydracrylic Acid.*—In the preparation of one sample of hydracrylic acid a very slight excess of sulphuric acid was used in liberating the hydracrylic acid. The hydracrylic acid, without purification from the trace of sulphuric acid, was esterified by boiling with a large excess of absolute alcohol for twelve hours without the addition of any catalysing acid. About two-thirds of the acid was esterified, but a relatively large proportion of the resulting ester proved to be acrylic ester. A second sample of hydracrylic acid free from sulphuric acid was esterified by boiling with a large excess of absolute alcohol in the presence of anhydrous copper sulphate prepared by the gentle ignition of crystallised copper sulphate, but not freed from the traces of sulphuric acid formed in the process of dehydration. Here again the esterification proceeded rapidly until about 70 per cent of the acid was esterified, but as before the result was a mixture of acrylic and hydracrylic esters. It seemed, therefore, necessary to avoid even very small amounts of mineral acids in the esterification of hydracrylic acid in order to prevent the formation of acrylic ester.

Wislicenus (*Ann. Chem. Pharm.*, clxiv., 181) suggested the use of the vapour from boiling absolute alcohol as an efficient dehydrating agent in esterification. The inefficiency of absolute alcohol alone, as well as that of absolute alcohol vapour passed through the reaction mixture, and the superiority of anhydrous copper sulphate as a dehydrating agent are shown in the following experiment:—32 grms. of hydracrylic acid free from sulphuric acid were first boiled, with a reflux condenser, with 200 cc. of absolute alcohol for three hours, giving 9.4 per cent of the theoretical yield of ester; at the end of six hours 17 per cent of the acid was esterified. Then the reaction flask was heated at  $110^\circ$  and absolute alcohol vapour passed through the reaction mass, giving at the end of two hours 40 per cent. of ester and after two hours more only 42 per cent of ester. The current of absolute alcohol vapour was then discontinued and about 30 grms. of anhydrous copper sulphate, free from sulphuric acid, were added and the reaction mixture gently boiled, giving after three hours 74 per cent. of ester, and after three hours more 83 per cent of the acid was esterified. The ester formed was found to be hydracrylic ester free from acrylic ester.

In another experiment 26.4 grms. of hydracrylic acid were gently boiled with 200 cc. of absolute alcohol in the presence of about 50 grms. of anhydrous copper sulphate freed from sulphuric acid by means of absolute alcohol. At the end of three hours 66 per cent of the acid was esterified, at the end of six hours 71.4 per cent, at the end of nine hours 83 per cent of the theoretical amount of ester was formed, and the boiling was discontinued. To remove the unesterified hydracrylic acid in this and in the previous experiment a little less than the theoretical amount of anhydrous sodium carbonate was added to the esterification mixture and the excess of alcohol was distilled off on the water-bath. The hydracrylic ester was extracted from the residue with dry ether and the ether distilled off on a warm water-bath, finally heating the water-bath to boiling. From the two experiments 53 grms. of crude hydracrylic ester were obtained, which on fractionation under diminished pressure yielded 45 grms. of ethyl hydracrylate boiling at  $95.5^\circ$  to  $96^\circ$  at a pressure of 20 mm. to 22 mm. The saponification equivalent of the ester so prepared was found to be 119, and the saponification equivalent calculated from the formula  $CH_3OH.CH_2.COOC_2H_5$  is 118. When the ester was dissolved in an equal volume of water and was treated

with phosphorus and iodine both  $\beta$  iodopropionic acid and  $\beta$  iodopropionic ester were obtained. The ester at 20° has a density of 1.059, and like lactic ester is soluble in water in all proportions. These properties were considered sufficient to identify the ester as pure ethyl hydracrylate. The ester has a faint ethereal odour, much less pronounced than that of lactic ester. It is unusually stable in water solution, hydrolysing very slowly in the absence of a catalysing acid or alkali.

**Hydrolysis of the Ester.**—Two and a half cubic centimetres of ethyl hydracrylate were dissolved in 250 cc. of decinormal hydrochloric acid and hydrolysed at 25°, 35°, and 45°. The course of the reaction was followed by titrating 25 cc. portions of the mixture at intervals, as fully described in previous papers (*Am. Journ. Sci.*, 1913, xxxv., 486). The results of the velocity measurements are recorded in Table I. In Table II. are recorded summary results obtained partly simultaneously with the reaction velocity measurements of ethyl hydracrylate and taken partly from the results obtained by Dean (*Am. Journ. Sci.*, 1913, xxxv., 486). A striking contrast appears between the effects of  $\alpha$ -hydroxyl and  $\beta$ -hydroxyl on the velocity of hydrolysis of the esters in acid solution. This retarding effect of the  $\beta$ -hydroxyl on the hydrolysis velocity of the ester was predicted by Dean (*loc. cit.*) for ethyl hydracrylate from his study of the hydrolysis of lactic ester, glyceric ester, and the esters of the oxybutyric acids. From an examination of the velocity constants of ethyl propionate, ethyl lactate, ethyl hydracrylate, and ethyl glycerate in Table II., it is obvious that the effects of  $\alpha$ - and  $\beta$ -hydroxyl groups on the hydrolysis velocity are independent of each other. By comparing the constants for ethyl propionate and ethyl lactate it is seen that a hydroxyl here produces a slight accelerating effect at 25°, which, however, falls off at the higher temperatures. The  $\beta$ -hydroxyl produces a very marked retardation in the hydrolysis velocity, as will be seen by comparing the constants for ethyl propionate and ethyl hydracrylate. This effect does not fall off materially at the higher temperatures, as is shown by the fact that the ratio of the constants of these two esters is very nearly the same at each temperature at which velocity measurements were made. The combined effect of  $\alpha$ - and  $\beta$ -hydroxyl groups on the hydrolysis velocity is shown in the constants for ethyl glycerate. If the slight accelerating effect of a hydroxyl and the very marked retarding effect of  $\beta$ -hydroxyl are both taken into account, we would expect the constants for ethyl glycerate to be but slightly larger than those of ethyl hydracrylate at 25°, the percentage of difference falling off slightly at the higher temperature. This expectation is fully borne out by the experimental results. At 25° the constants for ethyl glycerate is 13.5 per cent larger than that of ethyl hydracrylate, at 35° it is 7.9 per cent larger, and at 45° the difference is but 2.5 per cent. The velocity constants in Tables I. and II. were all calculated from the usual titration formula for first order reactions. The temperature coefficient for ethyl hydracrylate is 2.46 for 25 to 35° and 2.44 for 35° to 45°.

Ethyl hydracrylate was also hydrolysed in N.80 sodium hydroxide solution at 0° and at 25°, and the course of the reaction followed by the titration method fully described in Dean's paper (*Am. Journ. Sci.*, 1913, xxxv., 605) on the saponification of the esters of other oxyacids. These results are recorded in Table III., and are in accord with the results obtained for the esters of other oxyacids.

**Summary.**—1. Hydracrylic acid may be conveniently prepared from glycerin by introducing the following modifications into the older methods; oxidation of glycerin by fuming nitric acid, and formation of the calcium salt instead of the lead salt; liberation of the glyceric acid by means of oxalic acid, and conversion into  $\beta$ -iodopropionic acid with iodine and solid yellow phosphorus instead of a carbon disulphide solution of phosphorus; neutralisation of the  $\beta$  iodopropionic acid with sodium carbonate before removal of the iodine by the action of silver oxide; substi-

tution of hydroxyl for iodine in  $\beta$ -iodopropionic acid by acting on a concentrated solution of the sodium salt in the cold with silver oxide, using mechanical stirring, instead of treating the hot dilute solution of the free acid with silver oxide.

2. Hydracrylic acid, free from a mineral acid, may most conveniently be esterified by boiling with an excess of absolute alcohol in the presence of anhydrous copper sulphate free from sulphuric acid.

3. Hydracrylic ester boils at 95° to 96° under a pressure of 20 mm. without decomposition, but with decomposition at ordinary pressure. The ester has a density of 1.059 at 20° and is soluble in water in all proportions, but is hydrolysed only very slowly by water in the absence of a catalyst.

4. On hydrolysis in the presence of an acid catalyst the  $\beta$ -hydroxyl shows a very marked retarding effect on the velocity of the reaction, while in alkaline hydrolysis the  $\beta$ -hydroxyl produces a distinct accelerating effect.

TABLE I.—Ethyl Hydracrylate.

Hydrolysis in Decinormal Hydrochloric Acid.

	25°	35°	45°
Time of reaction in minutes	72.40	28.40	13.90
Velocity constants .. ..	10°K	10°K	10°K
	16.6	39.9	98.0
	16.6	39.8	98.6
	16.4	41.4	100.3
	16.0	40.4	97.9
	16.1	40.5	98.6
	16.6	39.3	98.9
	15.8	41.0	97.3
Averages ..	16.3	40.4	98.5
Averages of duplicate series	16.2	40.9	99.0

TABLE II.—Oxypropionic Esters; Summary.

Hydrolysis in Decinormal Hydrochloric Acid.

Temp.	Ethyl propionate. 10°K	Ethyl lactate. 10°K	Ethyl hydracrylate. 10°K	Ethyl glycerate. 10°K
25°	71.2 71.6 (a)	76.1 74.4 (a)	16.3 16.2	18.5 (a)
35°	177.1 179.0 (a)	177.5 179.0 (a)	10.4 40.9	43.6 (a)
45°	405.3 406.0 (a)	396.6 396.0 (a)	98.5 99.0	101.0 (a)

(a) Determined by Dean (*Am. Journ. Sci.*, 1913, xxxv., 486).

TABLE III.—Alkaline Hydrolysis in N.80 Sodium Hydroxide.

Ethyl Hydracrylate.

Temperature 0°. Time 30 min. Constant K.	Temperature 25°. Time 12 min. Constant K.
1.86	10.6
1.63	11.0
1.93	10.6
1.81	9.7
1.85	10.8
1.87	9.5
1.85	9.0
1.83	10.2

Summary.

	K (0°).	K (25°).
Ethyl propionate .. ..	1.16 (a)	5.94 (a)
Ethyl lactate .. ..	1.6 (a)	63.7 (a)
Ethyl hydracrylate .. ..	1.83	10.2
Ethyl glycerate .. ..	9.02 (a)	67.3 (a)

(a) Taken from Dean's tables (*Am. Journ. Sci.*, xxxv., 608).

## PHOTOGRAPHY IN COLOURS.

SOME beautiful photographic portraits in colours by the new Kodachrome process were shown for the first time in this country at a meeting of the Royal Photographic Society on Tuesday, the 9th inst.

*A New Two-Colour Method.*—Mr. George E. Brown, F.I.C., Editor of the *British Journal of Photography*, describing the process, said that two plates sensitised for all colours are exposed in the camera either simultaneously or in quick succession, one through a red filter and one through a green filter. These plates are developed and fixed in the usual way, after which the black silver forming the image is removed by simple chemical means. The plates are then dyed—that taken through the red filter in a green dye, and that taken through the green filter in a red dye. The plates take up the dyes in inverse proportion to the original silver deposit. They are then brought face to face and bound up in register, the combination of the two-colour images by transmitted light giving a remarkably fine reproduction of the original.

*Beautiful Flesh Tints.*—The delicate flesh tints are particularly well rendered, and the entire absence of mechanical screen rulings and dots is a great advantage. The pictures consist entirely of colour, and the particular point of interest to the student of colour processes is the successful solution of the problem of converting the "red" and "green" record negatives directly into "green" and "red" colour positives respectively.

*Commercial Possibilities.*—That the new process has a very promising commercial future is clearly shown by the unqualified success with which American professional photographers have applied it to studio portraiture.

*Any Number of Copies.*—Considered commercially, an important aspect of the process is the fact that any number of copies can be reproduced from the original pair of negatives. In that case the original negatives are preserved as negatives, master glass positives being made from them by contact in the usual way, and from them the required number of negative duplicates which are freed from the silver and dyed as already outlined. Reproductions so made shown in company with originals fully held their own.

*Full Scope for Re-touching.*—Apart from the extraordinary rendering of the colours, the process possesses the fundamental advantage that the plates can be re-touched, etched, and air-brushed, so that a skilful, artistic operator has full scope for his abilities and is not limited by a machine like process, as when working any of the earlier processes.

## PROCEEDINGS OF SOCIETIES.

## ROYAL SOCIETY.

Ordinary Meeting, March 11, 1915.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Contributions to the Study of the Bionomics and Reproductive Processes of the Foraminifera." By E. HERON-ALLEN.

"Occurrence of an Intracranial Ganglion upon the Oculomotor Nerve in Scyllium Canicula, with a Suggestion as to its Bearing upon the Question of the Segmental Value of certain of the Cranial Nerves." By G. E. NICHOLLS.

"Experiments on the Restoration of Paralyzed Muscles by means of Nerve Anastomosis. Part III. Anastomosis of the Brachial Plexus, with a Consideration of the Distribution of its Roots." By Prof. R. KENNEDY.

"Mechanism of the Cardiac Valves." (A Preliminary Communication). By A. F. S. KENT.

## NOTICES OF BOOKS.

*The Chemistry of Petroleum and Its Substitutes.* By C. K. TINKLER, D.Sc. (Birm.), B.Sc. (Lond. and Wales), and F. CHALLENGER, Ph.D. (Göttingen), B.Sc. (Lond.), F.I.C. With an Introduction by Sir BOVERTON REDWOOD, Bart. London: Crosby Lockwood and Son. 1915.

THIS book was primarily intended to be used as a handbook by the students attending the three years' course in petroleum mining recently instituted by the University of Birmingham, but it will undoubtedly be found equally useful by a much wider circle of readers. The authors have done their utmost to emphasise the fundamental importance for the technologist of a thorough training in pure science, and a large part of the book is occupied with the pure chemistry of petroleum. While being, perhaps, somewhat difficult for the use of the student who has no knowledge whatever of organic chemistry, it provides a very thorough grounding in the subject, and the course of practical work described is excellent for the purpose. It includes preparations of important compounds, the determination of physical constants, flash-points, &c., and chapters on practical distillation and crystallisation. Methods of preparing and denaturing alcohol are dealt with at some length, the authors being convinced that in the future large quantities of it will be used as a substitute for petrol.

*The Extra Pharmacopœia of Martindale and Westcott.* Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M.B.(Lond.), D.P.H. Sixteenth Edition. In Two Volumes. London: H. K. Lewis. 1915.

IN preparing the last edition of the extra Pharmacopœia the matter has been re-arranged, and much information relating to new drugs and methods of treatment has been added. Thus, to mention only a few of the alterations, the uses and properties of many new anaesthetics and vaccines are discussed, and the chapter on organic arsenic compounds has been revised. A good deal of attention is paid to the uses of colloidal metals, and many new tuberculin treatments are noted. The bacteriological examination of drinking-water is shortly treated, and bacteriological and clinical notes referring to special diseases have been added.

*The Hydrogenation of Oils.* By CARLETON ELLIS, S.B. London: Constable and Co., Ltd. 1914.

THE recent important discovery of commercially practicable methods of hydrogenating and thus hardening oils will undoubtedly find very extensive industrial application, and this book, in which the subject is treated very comprehensively, will be valuable both to students and practical workers. The author has brought together all the information he could gather about patents and processes. He has not attempted to criticise the data collected, but has merely given detailed accurate descriptions, without comments, of the patents of all nations, with as many particulars of plant, output, &c., as he could obtain. The properties and preparation of different catalysts are fully discussed, as well as the uses of hardened oils in soap making and for the preparation of edible products, while chapters on industrial methods of obtaining hydrogen deal very fully with all the chief processes.

## MEETINGS FOR THE WEEK.

MONDAY, 29th.—Royal Society of Arts, 8 (Cantor Lecture). "House Building," by M. H. Baillie Scott.

WEDNESDAY, 31st.—Society of Public Analysts, 8. "Estimation of Methyl Alcohol in presence of Ethyl Alcohol," by G. Cecil Jones. "Determination of Niobium in presence of Tantalum, and some Reactions of Tantalum Compounds," by A. G. Levy. "Estimation of Carbon Dioxide in Self-raising Flours and Baking Powder," by T. Macara. "Bromine Method of Determining Phenol," by W. Versfeld. "Method for the Determination of Chlorine in Cheese," by Miss E. C. V. Cornish and J. Goulding.



# THE CHEMICAL NEWS.

VOL. CXI., No. 2888.

## THE CYCLIC EVOLUTION OF THE CHEMICAL ELEMENTS.

PART I.

By F. H. LORING.

SIR WILLIAM CROOKES's well-known conception of the elements having been evolved out of some primary matter under the influence of Time and Temperature connected with Electricity is doubly suggestive at the present period, now that the atom is supposed to be made up of positive and negative electrons. In the words of his Presidential

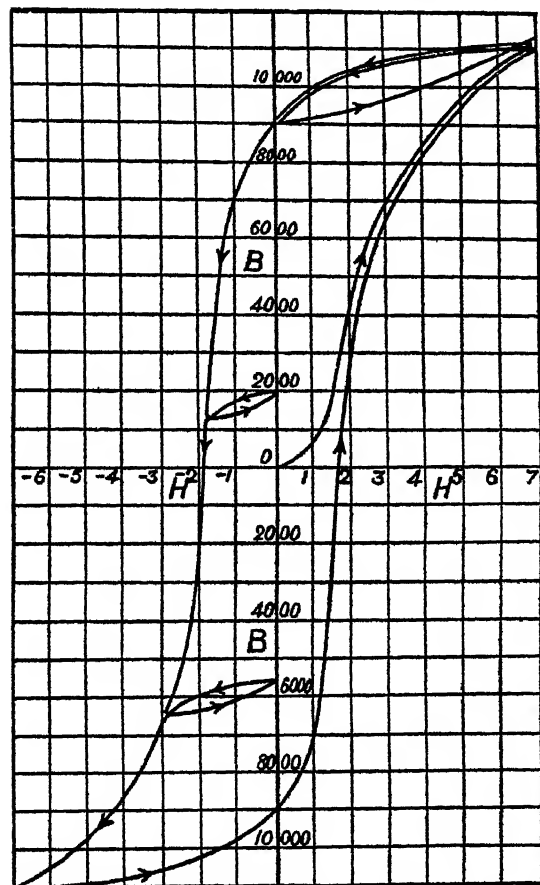


FIG. 1.

Address before the Royal Society (November 30, 1914; CHEMICAL NEWS, cx., 287) he says:—"I ventured to suggest a possible explanation of these facts,\* based on the assumption that acting on the original *protyle* were two forces—one of the character of Time, accompanied by a lowering of temperature, while the other, swinging to and fro like a pendulum, and having periodic cycles of ebb and flow, rest and activity, would be intimately con-

nected with the force of electricity. I arrived at a presentation of the elements on a lemniscate path which seemed to me to throw some light on the question of their genesis."

If we now adopt as a general basis for the evolution of the elements Sir William Crookes's idea of ebb and flow, &c., under electrical influence, it is perhaps best to select as a specific starting point some known phenomenon of a cyclic character which involves molecular action. The hysteresis loop seems the most suggestive in its peculiar cyclic representation of varying molecular changes. We are, of course, reminded of the Ewing (-Warburg) theory of this phenomenon.

The following inquiry takes, therefore, the form of an argument in favour of representing the *evolution* of the chemical elements by means of a cyclic diagram, similar to a complex hysteresis loop indicating changes in magnetism when the magnetising force is periodically withdrawn and re-applied during its general progressive variation. Moreover, such a figure is essentially an energy cycle, and thus we keep in the foreground the idea of work being performed in the process. The word hysteresis, it will be remembered, is from *hysterein*, to lag behind.

If we take a proper diagram out of Prof. Ewing's book, "Magnetic Induction in Iron and Other Metals," third edition published—one showing a typical hysteresis loop, and a second one showing a number of smaller side loops due to interruptions in the continuity of the applied magnetising force, or, to avoid unnecessary repetition of diagrams, if one be selected from page 95, showing both types of loops—by analogy the element formation might be represented as a similar *cyclic process*. The diagram referred to is reproduced in Fig. 1.

The analogy is thus far obviously imperfect, but by attempting a comprehensive representation it may be

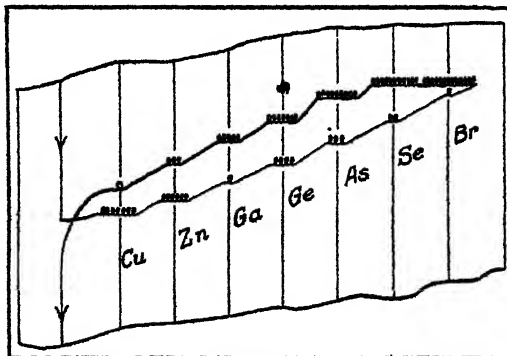


FIG. 2.

developed so as to take into account a number of characteristics peculiar to the elements.

Therefore we may assume that elements can be formed when there are *time breaks* or "rests" in the continuity or activity of the flow of energy, in the sense that when the impelling or accelerating force (taken apparently as passing from positive to negative) is withdrawn and re-applied, or a sudden change is made in it, a new phenomenon asserts itself, as if the stored or impressed energy had creative power to form certain elements.

Then, expanding this idea, it seems reasonable to illustrate a single offshoot or subordinate loop from a general curve, in such a way that the former will have horizontal parts or steps, representing *times* during which elements (atoms) were condensed or formed, and the sloping or more or less vertical parts indicate the activity referred to.

It is in keeping with this idea to go a step further, and assign to the flat portions of the curve varying lengths in representation of varying time periods of "rest." These periods, moreover, may be made to correspond to the relative numbers of associated component atoms formed,

\* See original, as I have altered the setting of the quotation, the facts referred to not being detailed here.—F. H. L.

assuming that the conception of "associates" is one having some representation in fact (see CHEMICAL NEWS cited below).

Having proceeded so far with the argument, it will make things realistic if, instead of straight-line flats, some curls be introduced to represent the elements or atoms, as if the energy took some vortex form and detached itself in forming them. This result is now shown by Fig. 2.

We must remember that the present trend of scientific revelation is towards natural or fundamental units, or quanta of heat, light, and energy generally. Electricity, in the case of the so-called negative "state," has been experimentally found to be granular: to comprise definite quanta termed electrons. The mass of the electron has been interpreted as being partly or even wholly electromagnetic. The corresponding positive electron, which has for a long time been most elusive, is now regarded in some quarters as the hydrogen atom, or, to speak more accurately, the nucleus of the atom without its normally attendant electron. Indeed, Sir J. J. Thomson has been able to detach from the hydrogen atom one negative electron, "the only one it had." See "The Atomic Theory" (the Romanes Lecture, 1914, by Sir J. J. Thomson, p. 18, published by the Clarendon Press). It is further supposed on good

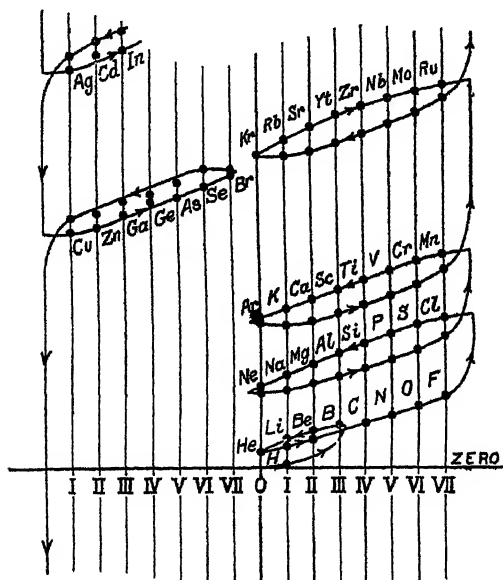


FIG. 3.

grounds that all the elements are formed out of the "stuff" of hydrogen, and the number of attendant electrons, which varies from element to element (considering the atoms of different elements), has been roughly evaluated.

The radio-elements disintegrate principally by giving off either helium atoms, or electrons only in some cases. The helium unit may thus be an exceedingly stable configuration of four hydrogens, with, however, only two apparent negative electrons. This would make the atom, taken as an alpha-particle, have two positive charges in excess. This brings us back to the well-known Prout hypothesis in so far as the elements (atoms) may be stable polymerides of hydrogen, but the number of "internal" and "external" negative electrons associated with the nucleus of each element is still awaiting further investigation; that is to say, we may expect the specification that has been drawn up for some elements to be extended. The external electrons are supposed to give rise to chemical activity; to exercise, in fact, valency functions.

Referring to Fig. 2, the number of curls correspond, we assume, to the atom-numbers (see CHEMICAL NEWS, cxii, 13, and previous citations therein). The conception of "curls" gives the period of rest an activity, so that we may require to modify our terms as we proceed with the argument.

We may observe that a complete offshoot has the curl or loop characteristic of a single "atom-vortex," so that a series or row of elements collectively, in a sense, simulates the individual members. So far, the largest relative number of proper associate atoms of equal weight appears to be thirteen or fourteen, which is about equal to the number of two-part groups (fourteen) in an arrangement or special classification given in "Studies in Valency," p. 23 (Simpkin, Marshall, and Co.), suggesting that there are number-limitations, which is consistent with the idea of "duplication." Referring to the peculiarities of the "associates," there are supposed to be two types, just as there is duality in the group arrangement cited.

The subordinate loops under consideration, as representing certain series of elements, involve an upper and lower line on which the associates take their place, and these small intermediate loops or offshoots simulate the larger main one, just as the atom-vortices partake of the characteristics of the former, as already mentioned. It seems to suggest vaguely a principle of successive subordinate types or processes.

There are, however, elements which appear not to be composite, in that their atomic weights are not mean values derived from differing proportionate numbers of integer elements whose atomic weights differ. They appear to be whole-number elements (atoms) without atomic weight variation in this respect (see CHEMICAL NEWS, cx., 169).

To account for these various peculiarities, and to keep as far as possible to a cyclic diagram, one has been prepared, as shown by Fig. 3, in which the vertical distances represent roughly atomic weights and the horizontal spacings the group-places. Only a portion of the elements are arranged in this manner.

The diagram does not take all the elements falling within the area shown, so that another system may exist. These diagrams involve too much uncertainty to be satisfactorily carried out to completion; indeed the "associates" shown on the right-hand half are quite arbitrarily evaluated, no very accurate representation being attempted. Fig. 2 is regarded as a detail representation of Fig. 3 in part, one loop being taken by way of example.

The comparison of these diagrams with those characterising various manifestations of hysteresis phenomenon should certainly awaken interest in Sir William Crookes's idea of the genesis of matter, but it would be a mistake to push the analogy too far. We already see difficulties in choosing such terminology as will enable us to pass from one phenomenon (hysteresis) to the other (evolution of the elements) without the possibility of involving ourselves in wrong interpretations of known facts concerning either the elements themselves or the magnetic effects studied.

The above considerations really involve us in wider ones; in particular, the problem of matter in regard to its states. The vacuum tube has revealed substance in a primitive form, and it was supposed by Crookes that this represented an ultra-gaseous or fourth state of matter, an idea that seems generally accepted. Relatively, the so-called vacuum tube state is a fourth state, but by starting the order of reasoning at a different point in the circle of events and introducing geometrical and physical ideas, we arrive at the conception of tri-dimensional matter which does not give us fully recognisable substance, or the full embodiment, if we may so express it, and it is to the fourth state that we perhaps owe this property, though we cannot give adequate expression to the physical reality of things thus arrived at.

If we now turn to the "Theory of Relativity" (1914), by Silberstein, p. 134, we find the following:—"H. G. Wells: 'The Time Machine,' 1898 (Tauchnitz Edition),

p. 13. It is interesting to remark that even the forms used by Minkowski to express these ideas, as 'Three-dimensional geometry becoming a chapter of the four-dimensional physics,' are anticipated in Mr. Wells's fantastic novel. Here is another sample (*loc. cit.*, p. 14) illustrative of what is now called a world tube:—'For instance, here is a portrait [or, say, a statue] of a man at eight years old, another at fifteen, another at seventeen, another at twenty-one, and so on. All these are evidently sections, as it were—Three dimensional representations of his Four-dimensional being, which is a fixed and unalterable thing.' Thus Mr. Wells seems to perceive clearly the absoluteness, as it were, of the world-tube and the relativity of its various sections." Time as a "dimension" is the root principle of this idea, and in order to show space relations it is regarded mathematically as a fourth-dimensional axis in a system having three axial coordinates— $x$ ,  $y$ , and  $z$ . We may note in passing that Dr. Silberstein's work is mathematical.

Thus we may imagine that the elements, though possibly evolved out of whirls of energy,\* have yet been impressed with some Time Influence, whereby they have passed from the infra- or ultra-material state into the fourth state, having then all the properties we associate with common things; for example, having weight; and in consequence perhaps the ratio of mass to weight has become unity.

## THE SEPARATION OF THE ILLUMINANTS IN MIXED COAL AND WATER GAS.†

By G. A. BURRELL and I. W. ROBERTSON

(Concluded from p. 152).

### Fourth Series of Fractionations.

AFTER removing the propylene and propane there remained a residue of 2.3 cc., only 0.11 per cent of the original quantity of gas (2048.0 cc.). This residue was analysed by burning it in oxygen, and the contraction and carbon dioxide calculated to butylene. The observed data are given in Table IV.

TABLE IV.—Analysis of Butylene Residue.

	Cc.
Volume taken for analysis..	2.3
Oxygen added ..	93.81
Total volume ..	96.11
Volume after burning..	90.53
Contraction produced..	5.58
Volume after KOH absorption..	82.86
Carbon dioxide produced by burning	7.67

According to the reaction  $C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$  there result three volumes contraction and four volumes carbon dioxide when butylene reacts with oxygen. The contraction and carbon dioxide observed in the above analysis, 5.58 cc. and 7.67 cc., is almost in the ratio of 3:4 within the error of making the analysis; hence the data was calculated to butylene. Such a small quantity of gas was available to work upon that there might easily have been a trace of butane present. However, the total quantity compared to the original volume was only 0.11 per cent, or practically insignificant. Benzene that

should have appeared in this last fraction did not show up; hence the inference is that in the many transfers of gas it had condensed in the pump, and removed a trace at a time in the other fractions and in sweeping out the pump with air.

The total number of cc. of gas from the various fractions =  $1782 + 167 + 21.1 + 2.3 = 1972.4$  cc. This is exclusive of the benzene. The benzene as found by using a separate portion of the coal gas is 1.33 per cent of the coal gas. Then  $2048 \text{ cc.} \times 1.33 \text{ per cent} = 27.2 \text{ cc.}$ , and  $1972.4 \text{ cc.} + 27.2 \text{ cc.} = 1999.6 \text{ cc.}$ , or within about 5.0 cc. of the amount (1995 cc.) that was fractionated. Considering the number of times the different fractions of gas were handled and measured in the fractionation analysis this is not a bad check on the operation.

### Determination of Benzene.

For the benzene determination a separate quantity of gas was used, and advantage taken of an apparatus suggested by Dr. G. A. Hulett, chief chemist of this Bureau, for the determination of water-vapour in air. Dr. Hulett suggested that air with its moisture be cooled at the temperature of liquid carbon dioxide and the air be then removed with a mercury pump, and the water-vapour be determined after removing the cooling medium by measuring its pressure. It was a simple matter to apply this principle to the determination of benzene in coal gas. The procedure was to free the coal gas of carbon dioxide and water-vapour, and introduce it into the liquefaction bulb *b* (Fig. 1), cool it at a temperature of  $-78^\circ \text{C.}$ , and remove as much gas with the pump as possible. The stopcock *n* on the bulb was then closed, and the Dewar flask containing the cooling medium removed. The condensed liquid in the bulb then vaporised, and its pressure read on the manometer *j* (Fig. 1). This pressure compared to the original pressure of the gas gave the percentage of benzene in the coal gas. The results of two determinations are shown in Table V.

TABLE V.—Results of the Benzene Determination.

Original pressure of the gas (mm. of mercury) ..	744	744
Partial pressure of the benzene vapour (mm. of mercury) ..	10	9
Illuminants found in the distillate (percentage of the total coal gas)	7.32	7.39
Calculation of benzene ..	$\frac{10 \times 100}{744}$	$\frac{9 \times 100}{744}$
Percentage of benzene in the coal gas of Pittsburgh ..	1.34	1.31

The total illuminants in the gas of Pittsburgh as found by absorption in fuming sulphuric acid is 8.67 per cent (see *ante*). The distillate from the benzene determination was analysed by absorbing the remaining illuminants in fuming sulphuric acid. There was removed 7.32 and 7.39 per cent of the distillates. These amounts when added to the benzene found, 1.31 and 1.34 per cent, equal 8.66 and 8.70 per cent, or almost identically the same quantities as the total illuminants in the coal gas. Benzene reacts with oxygen as follows:— $C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O$ . The contraction is 2.5 volumes, and the carbon dioxide is 6 volumes. The data given in Table VI. show the results of analysis of the residual vapour that was held in the liquefaction bulb (Fig. 1) when the coal gas was cooled at a temperature of  $-78^\circ \text{C.}$  Before analysis the benzene vapour was diluted with air.

It will be observed that the ratio between the carbon dioxide and contraction is almost exactly 6:2.5, showing that the vapour obtained in the determination was benzene. Traces of other easily condensable vapours may have been present but apparently in such small quantity as to be negligible. The authors of this publication were unable to find the vapour pressure of benzene at  $-78^\circ \text{C.}$ , but apparently it is very small. Benzene boils at  $80^\circ \text{C.}$

\* We are reminded of Lord Kelvin's idea of atoms being formed as vortex rings out of the hypothetical ether. According to the Relativists, by the way, the theory of relativity abolishes the ether—to put it pointedly. Matter itself seems sufficiently endowed with remarkable properties to afford means of explaining all phenomena without recourse to an ether. The conception of a "proton" may be also regarded as equally speculative, but we see that this conception looks like common sense, now that experiment is bringing about a wider view of matter. When we come to understand more of matter in its various states we shall possibly abandon the ether.

† Presented at the meeting of the American Gas Institute, October 22, 1914, New York City, with the permission of the Director of the U.S. Bureau of Mines.

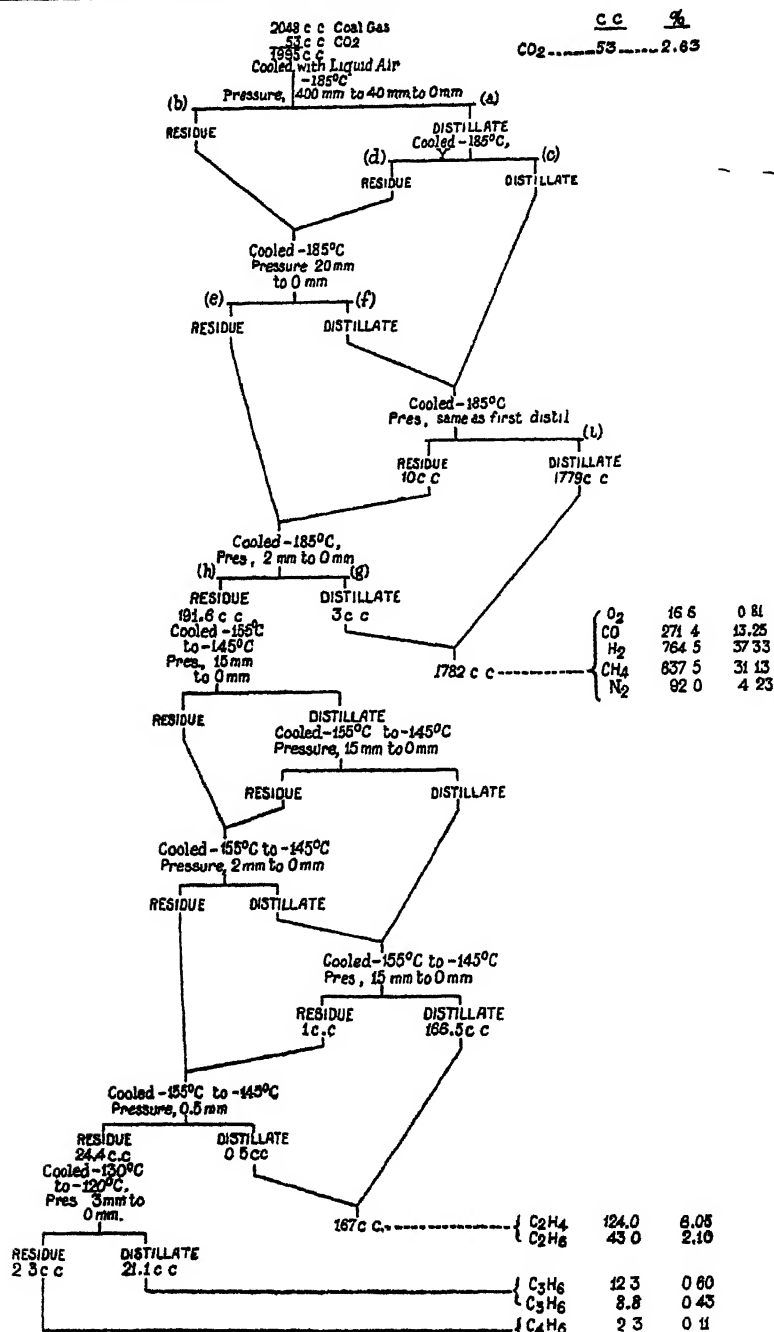


FIG. 2.

At -20° C. the tension is 5.76 mm. (Landolt and Bornstein, "Physikalisch-Chemische Tabellen," 1905, p. 143, according to Regnault). The authors prepared saturated vapours of benzene by shaking pure benzene with dry air. It was a simple matter to prepare unsaturated vapours of benzene by simply diluting the saturated vapours with air. The quantity of benzene in the air was checked by combustion analysis. A number of tests were made of the

benzene in air by the method just described. It was found that at -78° C. all of the benzene could be separated from the air. Analyses were made of the distillates and residues to make sure that all of the benzene remained in the liquefaction bulb at the temperature of -78° C. The foregoing method therefore seems to be well adapted for the benzene determination. There is needed a mercury pump, a liquefaction bulb, a gas burette for introducing

the gases, and Dewar flask for holding the refrigerant. A temperature of  $-60^{\circ}$  C. can easily be obtained by using the liquid carbonic acid sold in tanks. The coal gas does not even have to be measured and its exact volume determined. It is sufficient to introduce it into the liquefaction bulb at atmospheric pressure and then to read the barometer.

TABLE VI.—Analysis of Benzene Vapour.

	Cc.
Volume taken for analysis..	28.29
Oxygen added .. .. .	51.94
Total volume .. .. .	80.23
Volume after burning..	75.47
Contraction due to burning ..	4.76
Volume after KOH absorption..	64.25
Carbon dioxide produced by burning	11.42

*Complete Analysis of the Artificial Gas at Pittsburgh.*

The complete analysis of the artificial gas as found by the foregoing methods is given in Table VII.

TABLE VII.—Complete Analysis of Artificial Gas.

Constituent.	Formula.	Per cent.
Carbon dioxide .. ..	CO <sub>2</sub>	2.63
Oxygen .. .. .	O <sub>2</sub>	0.81
Carbon monoxide .. ..	CO	13.25
Hydrogen .. .. .	H <sub>2</sub>	37.33
Methane .. .. .	CH <sub>4</sub>	31.13
Ethane .. .. .	C <sub>2</sub> H <sub>6</sub>	2.10
Propane .. .. .	C <sub>3</sub> H <sub>8</sub>	0.43
Ethylene .. .. .	C <sub>2</sub> H <sub>4</sub>	6.05
Propylene .. .. .	C <sub>3</sub> H <sub>6</sub>	0.60
Butylene .. .. .	C <sub>4</sub> H <sub>8</sub>	0.11
Benzene .. .. .	C <sub>6</sub> H <sub>6</sub>	1.33
Nitrogen .. .. .	N <sub>2</sub>	4.23
Total .. .. .		100.00

*Analysis of a Different Sample of Artificial Gas.*

There is shown in Table VIII. the analysis of a sample of the artificial gas of Pittsburgh collected at a different date than the one already given. It is interesting as showing the marked uniformity of the gas collected on two days about seven weeks apart. The benzene was not determined in this analysis because the method had not been perfected.

TABLE VIII.—Analysis of a Sample of Artificial Gas at Pittsburgh made on July 10, 1914.

Constituent.	Formula.	Per cent.
Carbon dioxide .. ..	CO <sub>2</sub>	2.40
Oxygen .. .. .	O <sub>2</sub>	0.61
Carbon monoxide .. ..	CO	13.63
Hydrogen .. .. .	H <sub>2</sub>	37.13
Methane .. .. .	CH <sub>4</sub>	30.92
Ethane .. .. .	C <sub>2</sub> H <sub>6</sub>	1.92
Propane .. .. .	C <sub>3</sub> H <sub>8</sub>	0.32
Ethylene .. .. .	C <sub>2</sub> H <sub>4</sub>	6.36
Propylene .. .. .	C <sub>3</sub> H <sub>6</sub>	0.70
Butylene .. .. .	C <sub>4</sub> H <sub>8</sub>	0.12

*Heating Value of the Illuminants in the Gas of Pittsburgh.*

In calculating the heating value of artificial gas from the analysis as ordinarily made a value is usually assigned to the illuminants that is an approximation, because the constituents that make up the illuminants have not been exactly known. With these data at hand for the gas of Pittsburgh the authors show in Table IX. a value calculated from the complete analysis.

According to these calculations the illuminants have a heating value at  $0^{\circ}$  C. and 760 mm. of pressure of  $\frac{182.50 \times 100}{8.09} = 2141$  b.t.u. The authors have included propane in the illuminants as ordinarily determined by

absorption in fuming sulphuric acid because propane dissolves to a certain extent in the acid. Just how much is not known. It was found that the methane and ethane were soluble to a slight extent (see G. A. Burrell and F. M. Seibert, "The Sampling and Examination of Mine and Natural Gases," *Bulletin* 42, U.S. Bureau of Mines, p. 47). Unquestionably propane is much more so because the higher paraffins are more soluble than the lower ones. Excluding propane the heating value of the illuminants becomes  $\frac{173.2 \times 100}{8.09} = 2141$  b.t.u. per cubic foot at  $0^{\circ}$  C. and 760 mm. of pressure.

TABLE IX.—Showing the Heating Value of the Illuminants in Artificial Gas.

Constituents.	B.t.u. per cubic foot at $0^{\circ}$ C. and 760 mm. pressure (a).	Constituents present in the coal gas.	Heating value of the constituents present in the coal gas.
Ethylene ..	1673	0.0605	101.21
Propylene ..	2509	0.0060	15.05
Butylene ..	3265	0.0011	3.59
Benzene ..	4012	0.0133	53.36
Propane ..	2654	0.0035	9.29
		0.0844	182.50

(a) These heating values were calculated from the values as found by Thomsen. His values are given in Landolt and Börnstein's "Physikalisch-Chemische Tabellen," 1905, p. 425. They are given in large calories per gram-molecule.

*Additional Details of the Experiment.*

Temperatures higher than the temperature of liquid air were obtained by cooling a natural gas condensate. This condensate was obtained from a natural gas gasoline plant by subjecting natural gas (casing-head gas) from an oil well to a pressure of 250 pounds per square inch, and then cooling it to ordinary temperatures. A steel cylinder, such as is used in transporting oxygen, was shipped to the natural gas gasoline plant of the Bessemer Gas Engine Company at Follansbee, West Virginia, for the purpose of collecting the condensate. This condensate is known in the natural gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butenes, especially the latter, as well as some of the ordinary gasoline constituents, the pentanes, hexanes, &c. Ordinary refinery gasoline and other substances, such as alcohol, ether, methyl, and ethyl chloride, jellied so much at low temperatures that they could not be used satisfactorily. In order to obtain a temperature higher than the temperature of liquid air, say,  $-145^{\circ}$  C., the condensate was placed in a Dewar flask, and stirred with a test-tube into which liquid air was run until  $-145^{\circ}$  C. was reached. Upon removal of the test-tube containing the liquid air the condensate warmed up slowly, about  $5^{\circ}$  C. to  $10^{\circ}$  C. per hour, thereby affording sufficient time for the withdrawal of the vapours. If the condensate rose to a higher temperature than was desired it was a simple matter to introduce a little more liquid air, and cool it.

Temperature measurements were made with two pentane thermometers. They agreed with each other, and gave within  $1.5^{\circ}$  C. the true melting-points of chloroform and carbon disulphide, and the sublimation point of liquid carbon dioxide. Fresh liquid air, as it usually reached the laboratory from a plant near by, had a temperature of  $-193^{\circ}$  C.

The determination of hydrogen sulphide, acetylene, carbon disulphide, ammonia, &c., that might have been present in the gas was not attempted, because the method used is scarcely adapted to the estimation of the traces of these constituents that are present in coal gas.

Future work on the fractionation of artificial illuminating gas will cover the analyses of gas that is used in other



cities than Pittsburgh, and the separation of the illuminants in the coal gas before it is mixed with carburetted water gas, and in oil gas that is used to enrich water gas.

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## THE NITROGEN OF PROCESSED FERTILISERS.\*

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Scientist in Soil Fertility Investigations.

(Continued from p. 147).

### ISOLATION AND IDENTIFICATION OF DEFINITE COMPOUNDS FROM THE PROCESSED FERTILISER.

TEN pounds of base goods were extracted by boiling for one hour with 20 gallons of water in a steam-jacketed kettle. The solution was filtered from the insoluble residue, made exactly neutral with caustic soda, the precipitate formed filtered off, and the filtrate concentrated in a steam kettle to a volume of about 3500 cc.

This solution contained phosphates, sulphates, and much other mineral matter. In order to separate as much of these salts as possible from the organic compounds a cold saturated solution of barium hydroxide was added to the solution until no further precipitation took place. The heavy precipitate which formed was filtered off by suction, and washed many times with water. The filtrate was exactly neutralised with sulphuric acid and concentrated to a volume of about 2000 cc. After cooling, this solution was made acid to 5 per cent with sulphuric acid, and a solution of phosphotungstic acid was added to slight excess, and the mixture allowed to stand.

After three days the precipitate which formed was filtered off, and washed with water containing about 5 per cent sulphuric acid and a little phosphotungstic acid. The precipitate was carefully dissolved in 45 per cent caustic soda solution, using phenolphthalein as an indicator, and adding at no time more than two drops of the alkali solution. Water was added so that a volume of about 1500 cc. was reached, and barium hydroxide solution was added until the phosphotungstic acid was precipitated. After filtering off the barium phosphotungstate, the free alkali was just neutralised with sulphuric acid, and the solution was then evaporated almost to dryness with barium carbonate in order to expel all of the ammonia. The residue was taken up in about 1000 cc. of hot water, and filtered, and the precipitate washed with hot water. The filtrate was placed in a 5 litre flask, and treated while hot with solid silver sulphate, which was added slowly until the solution contained sufficient to give a yellow precipitate, when a drop was removed and tested with a solution of barium hydroxide. The solution was then filtered, and the separation of the three hexone bases was carried out according to the method of Kossel and Kutscher (*Zeit. Phys. Chem.*, 1900, xxxi., 106). The solution was cooled to 40° C., and saturated with finely powdered barium hydroxide. The precipitate which was formed was collected and stirred up in a mortar with solid barium hydroxide, when it was again filtered off and washed with barium hydroxide solution. This precipitate contains the silver salts of histidine and arginine, while the filtrate contains the lysine.

**Lysine.**—The above filtrate was acidified with sulphuric acid, and freed from silver with hydrogen sulphide. Lysine was precipitated from this solution as the phosphotungstate, and the free base was obtained by decomposing this salt with barium hydroxide. From a concentrated solution of the base, which was strongly alkaline in reaction and which showed no tendency to crystallise on standing, the picrate salt was prepared,

This compound showed the solubility, characteristic crystalline appearance, and properties of lysine picrate (Kossel, *Zeit. Phys. Chem.*, 1898, xxv., 180; 1899, xxvi., 586). When taken up in boiling water and allowed to crystallise slowly, it formed in rather large yellow prisms, but when in small amount the crystals assumed a fern-like appearance. The lysine was further identified by the preparation from the picrate of the hydrochloride salt,  $C_6H_{14}O_2N_2 \cdot 2HCl$ , and the platinum chloride salt,  $C_6H_{14}O_2N_2 \cdot H_2PtCl_6 + C_2H_5OH$  (Hedin, *Zeit. Phys. Chem.*, 1895, xxi., 299).

The silver precipitate which would contain the arginine and histidine was suspended in water acidified with dilute sulphuric acid, and broken up with hydrogen sulphide. The silver sulphide was filtered off, the sulphuric acid was removed with barium hydroxide solution, and after filtering the solution was made slightly acid with nitric acid. Silver nitrate solution was added until a test drop with barium hydroxide gave a yellow precipitate. Histidine was completely precipitated as the silver salt by the careful addition of barium hydroxide solution. The precipitate was washed with barium hydroxide solution until the washings ceased to give a test for nitrates.

**Histidine.**—The histidine silver was suspended in water acidulated with sulphuric acid, and treated with hydrogen sulphide. The procedure described by Kossel and Kutscher was followed, and the histidine was finally separated as the dihydrochloride salt. The method of obtaining this compound and the characteristic crystalline form of the dihydrochloride salt are sufficient to establish its identity as histidine (Schwantke, *Zeit. Phys. Chem.*, 1900, xxix., 492; Kossel, *Ibid.*, 1896, xxii., 182).

**Arginine.**—The method of isolating arginine is simply a further step in the method used in the isolation of histidine. Arginine was isolated first as the acid nitrate salt, which crystallised in the form of plates (see Gulewitsch, *Zeit. Phys. Chem.*, 1899, xxvii., 178), and was further identified by preparing the neutral nitrate salt and the copper nitrate salt both in characteristic crystalline form.

**Monoamino Acid.**—The filtrate from the phosphotungstic acid precipitate was made alkaline with barium hydroxide in order to remove the sulphuric and phosphotungstic acids, and filtered. The filtrate was concentrated and nearly neutralised with sulphuric acid. This slightly alkaline solution, about 500 cc. in volume, was treated by boiling with freshly prepared copper hydroxide, and was then poured into about 3000 cc. of 95 per cent alcohol and allowed to stand overnight, in order that the insoluble mineral matter might settle out. The deep blue alcoholic solution was then filtered, the insoluble salts re-dissolved in water, and re-precipitated by pouring into alcohol as before. The alcoholic solutions were combined and evaporated to dryness, the residue was taken up in hot water, and the copper removed by treatment with hydrogen sulphide. After filtering from the copper sulphide, the solution, which contained considerable colour, was boiled with animal charcoal. The filtered solution was made faintly alkaline with ammonia, and treated with freshly precipitated copper hydroxide, keeping the volume of the solution at about 1000 cc. The solution was filtered from the excess of copper hydroxide, and evaporated to dryness on the steam-bath. The solid residue was then scraped from the sides of the dish, and extracted in a Soxhlet extractor with absolute methyl alcohol until no further blue colour was imparted to the alcohol.

**Leucine.**—The alcohol insoluble portion was dissolved in a large volume of boiling water, and the copper removed with hydrogen sulphide. The solution was filtered, boiled down to a volume of about 50 cc., and treated with ammoniacal lead acetate until no further precipitation took place. The precipitate was washed with 95 per cent alcohol, and was finally decomposed with hydrogen sulphide after suspending in water. On concentration of a portion of this solution the characteristic crystals of impure leucine formed. These crystals separated in concentric nodules closely resembling fat, but which were

\* Bulletin No. 138, United States Department of Agriculture, Bureau of Soils.

composed of concentrically grouped highly refracting needles. These crystals were re-dissolved in water and added to the original solution, which was boiled up with animal charcoal until the colour disappeared. The leucine was then purified as before by the formation of the copper salt and the basic lead salt. On concentrating the solution obtained from this purification, crystals of pure leucine were obtained. These crystals formed in pearly scales, which somewhat resemble cholesterolin. When dry the crystals were light, had a satiny glossy appearance, and were not easily wet again with water. They were extremely soluble in hot water, and quite easily soluble in cold water. Leucine was further identified by the fact that it sublimed (Schwanert, *Liebig's Ann.*, 1857, cii., 224), and by the crystalline form and solubility of the copper salt (Hofmeister, *Liebig's Ann.*, 1877, clxxxix., 16), and by its two colour reactions with quinone (Wurster, *Centrb. Physiol.*, 1889, ii., 590), red with a solution of leucine and quinone and violet when in addition sodium carbonate was used.

**Tyrosine.**—The methyl alcohol solution of the copper salts was evaporated to dryness, and the residue taken up in water. The copper was removed with hydrogen sulphide, and the solution was boiled with animal charcoal. After filtering, the solution was concentrated, and long thin silky needles began to separate. These needles, which closely resembled tyrosine, were filtered off, and the filtrate further concentrated, when another crop of needles was obtained. These were filtered off and added to the first fraction, and were then extracted with boiling 70 per cent alcohol. The crystalline residue was re-crystallised from water a number of times, and dried on a porous plate. This compound crystallised in the stellate groups of long slender silky needles which are characteristic of tyrosine. These crystals were relatively insoluble in cold water (Erlenmeyer and Lipp, *Liebig's Ann.*, 1883, ccxix., 161), very insoluble in cold 90 per cent alcohol, easily soluble in hot water, and were tasteless, colourless, and infusible. The compound was further identified as tyrosine by the formation of the copper salt, which was rather insoluble in cold water and fairly easily soluble in hot water, by the fact that a solution of the compound gave a red colour when boiled with Millon's reagent (Millon, *Comptes Rendus*, 1849, xxviii., 40; Lassaigne, *Ann. Chim. Phys.*, 1830, [2], xlv., 435), and that a sulphonic acid prepared from the compound gave a violet colour with ferric chloride (Piria, *Liebig's Ann.*, 1852, lxxxi., 252).

**Purine Bases.**—Five pounds of base goods were boiled up with 10 litres of water, filtered, neutralised, and concentrated to a volume of about 2500 cc. The solution was made strongly alkaline with sodium hydroxide, and the purine bases were precipitated with Fehling's solution and dextrose according to the method of Balke (*Journ. Prakt. Chem.*, 1893, [2], xlvii., 537). The supernatant liquid was decanted from the copper precipitate, and this was washed, until free from alkali, with a solution of sodium acetate, by repeated decantations. The precipitate was filtered, freed from sodium acetate by washing with alcohol, and the copper removed by suspending the precipitate in water, and treating it with hydrogen sulphide. After filtering off the copper sulphide the solution was concentrated, and the purine bases re-precipitated by means of a solution of silver nitrate and ammonia. After washing with water the silver precipitate was boiled with 10 cc. of nitric acid, specific gravity 1.1, and filtered. From this solution, on cooling and standing, crystals were deposited which were filtered off.

The filtrate was diluted with water, made alkaline by the addition of ammonia, and a solution of silver nitrate added. No precipitate was formed, showing the absence of xanthine.

**Guanine.**—The precipitate from the nitric acid solution was washed with water, suspended in water, and decomposed with hydrogen sulphide. The solution was filtered and concentrated to about 10 cc., when strong ammonia was added, producing a white gelatinous precipitate which

was filtered off and washed with a little cold water. The precipitate was dissolved in a little warm hydrochloric acid and tested for the presence of guanine by means of the xanthine reaction and Weidel's test, both of which were positive. From the remainder of the solution the characteristic picrate of guanine described by Capranica (*Zeit. Phys. Chem.*, 1880, iv., 233) and the dichromate described by Wulff (*Ibid.*, 1893, xvii., 477) were prepared. The method of obtaining this base, its solubility in water, ammonium hydroxide, and hydrochloric acid, the solubility of the silver salt in nitric acid (sp. gr. 1.1), the colour reactions, and the formation of the two characteristic salts—the picrate and dichromate—are sufficient to establish the identity of the compound as guanine.

**Hypoxanthine.**—The filtrate from the ammonia precipitation of guanine was boiled to expel all the ammonia and to a portion of the solution a solution of picric acid was added, but no precipitate was immediately formed, showing the absence of adenine. To another portion of the solution hydrochloric acid was added and the solution was concentrated, when crystals resembling those of hypoxanthine hydrochloride separated out in whetstone-like crystals or bunches of prisms. Hypoxanthine forms a characteristic silver nitrate salt (Neubauer, *Zeit. Anal. Chem.*, 1867, vi., 34) and a characteristic silver picrate salt (Bruns, *Zeit. Phys. Chem.*, 1890, xiv., 555), both of which are crystalline and relatively insoluble in water. Hypoxanthine does not give the xanthine reaction, but when treated with nitric acid and bromine water a yellow colour is produced, which on addition of sodium hydroxide turns red, and on heating acts like the xanthine reaction. By means of these reactions the substance was identified as hypoxanthine.

#### THE CHEMICAL CHANGES INVOLVED IN PROCESSING.

The compounds which were isolated from the base goods are tabulated in Table IV., according to the sources from which they have been derived and the chemical groups to which they belong. While it was not possible to isolate these compounds in a strictly quantitative manner, nevertheless it was evident that the purine bases were present in exceedingly small quantities, although the method used in their isolation was subject to no more error than some other of the isolation methods; this would indicate that the nitrogen of the purine bases makes up but a small percentage of the total nitrogen present in the fertiliser.

TABLE IV.—Organic Compounds Isolated from Sample of Base Goods.

Compound.	Chemical group.	Source of compound.
Arginine . . .	Diamino acids or hexone bases.	Products of protein hydrolysis by acid treatment of raw materials.
Histidine . . .		
Lysine . . .		
Leucine . . .	Monoaminoacids.	Plant constituent, or product of hydrolysis of nucleoprotein.
Tyrosine . . .		
Guanine . . .	Purine base . . .	Plant constituent, or product of conversion of nucleoprotein base.
Hypoxanthine .	Purine base . . .	Plant constituent, or product of conversion of nucleoprotein base.

**Purine Bases.**—It will be noticed that the two purine bases are listed in the table as coming from different sources. It is a well-known fact that the purine bases may exist in plant tissues and plant extracts as such; that is, they are not linked up in more complex compounds in such a way that their peculiar chemical identity is lost. In the garbage which has entered into the manufacture of the fertiliser, there were doubtless many sorts of plants or plant remains which contained some or all of the purine bases, and this fact alone would account for the presence of hypoxanthine and guanine in the finished product. This, however, is not the only source of the purine bases,

Levene and his associates have demonstrated that some of the purines enter into the composition of the nucleic acids, which are decomposition products of nucleo protein, and that they may be obtained by a process of hydrolysis from these nucleic acids (Levene and Jacobs, *Ber.*, 1911, xlv., 746; *Biochem. Zeit.*, 1910, xxviii., 127; Levene, *Abderhalden's Biochem. Arbeitsm.*, 1910, ii., 605; 1911, v., 489). Of the four purine bases commonly encountered, only guanine and adenine have been found to be constituent parts of the nucleic acid molecule, it matters not whether the nucleic acid be a decomposition product of animal or plant nucleoproteins. But it has been shown that the two purines found in the nucleic acids may be changed, both by chemical and biochemical agencies, into the two other purine bases, xanthine and hypoxanthine, so that these are frequently encountered. Thus, by the treatment of guanine with nitrous acid, Fischer (*Liebigs Ann.*, 1882, ccxv., 309) changed it into xanthine, and in the same manner Kossel (*Zeit. Phys. Chem.*, 1886, x., 258) changed adenine into hypoxanthine. Furthermore, Schittenhelm and Schröter (*Zeit. Phys. Chem.*, 1904, xli., 284), have shown that the putrefactive bacteria, especially the colon bacillus, were able to convert adenine and guanine into hypoxanthine and xanthine. They also show that the bacteria have the power of splitting the nucleic acid itself. This same change is also brought about by the action of certain enzymes, such as erepsin, on nucleic acid.

With these facts at hand it is possible to draw the following conclusions as to the source of the two purine bases in this fertiliser:—The guanine and hypoxanthine may be derived from plant remains which originally contained these two compounds; the guanine may arise by the acid hydrolysis of certain vegetable or animal nucleo-proteins which were present in the original materials; and the hypoxanthine may have been formed by the processes of natural decomposition, such as the action of bacteria and enzymes, which had taken place in the crude materials before they were subjected to the acidulation process or during the process itself. It is not improbable that the guanine and hypoxanthine come from all of these sources.

**Diamino Acids.**—Of the three diamino acids lysine was obtained in much the largest amount, arginine next, and histidine in the smallest amount. These compounds are products of protein hydrolysis by acids, but may also be produced under certain conditions by the action of bacteria. Since one or more of the diamino acids have been found to be present in every protein so far examined, and since the method for the analysis and the isolation of these bases is almost quantitative, the determination of the number and amounts of the diamino acids present in a mixture of protein hydrolysis products is of importance in deciding the nature and character of the original material which entered into the processed goods.

(To be continued).

## BRITISH SCIENCE GUILD.

### THE PROVISION OF GLASS APPARATUS FOR EDUCATIONAL PURPOSES.

#### JOINT REPORT OF THE EDUCATION AND TECHNICAL EDUCATION COMMITTEES.

**Technical Education Committee.**—Prof. Meldola, F.R.S.; Dr. Beilby, F.R.S.; Prof. R. A. Gregory; T. C. Horstall; Surgeon-General Sir A. Keogh, K.C.B.; Prof. Liversidge, F.R.S.; Sir Philip Magnus, M.P.; Prof. J. Perry, D.Sc., F.R.S.; Sir William Ramsay, K.C.B., F.R.S.; J. H. Reynolds, M.Sc.; Dr. A. Shadwell, M.A., LL.D.; Mrs. W. N. Shaw; Prof. Wertheimer; Right Hon. Sir William Mather, P.C., LL.D.; Sir Norman Lockyer, K.C.B., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; Dr. F. Mollwo Perkin; Lieut.-Colonel Sir Charles Bedford, D.Sc.

**Education Committee.**—Hon. Sir J. Cockburn, K.C.M.G.; J. Wilson, M.Sc.; Charles Bathurst, M.P.; Fred Charles, B.A.; J. Easterbrook; E. Gray; Prof. R. A. Gregory; E. G. A. Holmes; Sir Philip Magnus, M.P.; C. T. Millis; A. T. Pollard; Prof. T. Rayment; Miss C. E. Rigg; J. J. Robinson; Dr. R. M. Walmsley; Sidney Webb, LL.B.; Sir James Yoxall, M.P.; Right Hon. Sir W. Mather, P.C., LL.D.; Sir Norman Lockyer, K.C.B., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; Dr. F. M. Perkin; D. Berridge; and Dr. Tripp.

In the past practically all the glass and porcelain apparatus used in chemical laboratories in this country has been manufactured in Germany and Austria. As the supply is now cut off and the stocks held by British dealers are almost exhausted, the problem of obtaining apparatus for educational and technical purposes has become a serious one.

The Joint Committee is informed that efforts are now being made by several firms to introduce the manufacture of glass apparatus into this country, and being in hearty sympathy with these efforts, it has considered in what way the British Science Guild may best assist. In these efforts the Committee has co-operated with the Association of Public School Science Masters, and has taken action along two main lines, viz.:—

1. Endeavouring to obtain assurances of support for British makers of educational glass ware after the war as well as now.
2. Obtaining information from educational institutions respecting the principal types and sizes of glass apparatus in greatest demand.

#### 1. Assurances of Support for British Makers of Scientific Glass Ware.

It is understood that the efforts during the last three months by certain British glass manufacturers have been attended with satisfactory results as regards the quality of the products. Economic and manufacturing conditions have prevented British glass apparatus being sold at so low a price as has been paid in the past for German material. As these conditions will probably remain unchanged, British manufacturers have been naturally disinclined to expend the necessary capital in establishing the proposed new industry here, while there is every likelihood that they will be undersold in the British market by their competitors when the war is over. The Joint Committee is informed that this has acted as a strong deterrent to British glass manufacturers contemplating the production of scientific glass apparatus.

The Joint Committee, therefore, has endeavoured to ascertain how far it is probable that educational institutions would undertake to buy only British-made glass and porcelain apparatus during the war and for a period of three years after.

Inquiries were made in this direction by the Hon. Secretary of the Association of Public School Science Masters, who is a member of the Joint Committee, from the Head Masters of all schools represented on the Head Masters' Conference. Out of the 110 schools so represented, no fewer than 78, i.e. 71 per cent, have definitely promised to authorise their Science staffs to purchase as far as possible only British-made glass apparatus during and for a period of three years after the conclusion of the war. As these promises have been received from almost all the largest schools, both boarding and day, it may be assumed that manufacturers as well as dealers will receive adequate support from the "Conference schools."

The Guild also issued about 750 letters of inquiry to—

- (a) Local Education Authorities.
- (b) Governors of secondary schools.
- (c) Governing bodies of technical institutions.
- (d) Senates of Universities and University Colleges, and has received a very large number of replies.

The proportion of definite replies coming in at once has been smaller than in the case of the public schools, from the fact that various committees have had to be consulted before definite promises could be given, but the replies which have been received have been quite satisfactory. Of the definite replies received about 72 per cent are sympathetic, and promises are given to purchase only British-made apparatus as requested, subject in many cases to the proviso that the increased cost is not prohibitive.

A considerable number of the replies, while generally sympathetic, give no guarantee, the reason being in most cases that the matter rests with a higher authority, such as a county council or board of governors, from whom no definite reply had been obtained. Some authorities, also, while sympathetic do not feel able to bind their successors, and one authority suggests that only the purchase of German and Austrian apparatus should be barred.

The endeavour to obtain the value of the apparatus used in such institutions has not resulted in any very precise information, but from the facts before the Committee it is clear that the value of such apparatus must at least run to some thousands of pounds.

#### 2. Types and Sizes of Apparatus most in Demand.

Inquiries as to the principal types and sizes of apparatus most generally used have been made on behalf of the Joint Committee from public schools and technical schools. It was felt by the Joint Committee that this information would be of considerable value to glass makers, as there is a very strong feeling among those concerned with the chemical apparatus trade that at the present time flasks, beakers, basins, &c., are supplied in an unnecessarily large variety of shapes and sizes.

Judging from the replies received from the institutions above referred to, the following represent the apparatus most in demand:—

**Test Tubes.**— $6 \times \frac{1}{2}$  in.,  $2 \times \frac{1}{2}$  in., and, in smaller quantities,  $6 \times \frac{1}{2}$  in.,  $5 \times \frac{1}{2}$  in., and  $2 \times \frac{1}{2}$  in.

**Beakers.**—Squat form, lipped, 200 cc., 300 cc., and in smaller quantities, 150 cc., 500 cc., 1000 cc.

**Beakers.**—High form, in the same sizes as above but in smaller quantities.

**Flasks.**—Flat bottom, 100 cc., 250 cc., 500 cc., and in smaller quantities, 1000 cc., 1500 cc., 2000 cc.

**Flasks.**—Round bottom, 250 cc., 500 cc.

**Tubulated Retorts.**—150 cc.

**Funnels.**—5.5 cms.

**Distilling Flasks.**—100 cc., 250 cc., 500 cc.

**Evaporating Dishes.**—50 cc., 100 cc., 200 cc., and in smaller quantities, 1000 cc. and 2000 cc.

**Crucibles.**—15 cc. and 25 cc.

In conclusion, the Joint Committee desires to express its strong conviction that every effort should be made to facilitate and encourage the manufacture of glass and porcelain apparatus in the United Kingdom. It therefore urges the advisability of asking the Board of Trade to watch the new industry, and, if necessity should arise, to use its endeavours to modify any restrictions at present existing which may be detrimental to the carrying on and extension of the industry.

#### NEW BRITISH INDUSTRIES.

In order both to acquaint consumers with new sources of supply and to obtain support for new industries, the University of Sheffield Scientific Advisory Committee have just held, on March 18, 19, and 20 an exhibition of apparatus and material of British make. The following firms sent exhibits:—

Messrs. British Laboratory Ware Association (exhibiting through Mr. J. Preston, Sheffield).—Glass beakers, flasks, funnels, gas jars, tubing, porcelain crucibles, and basins of various makes, filter-papers from different sources, thermometers, and hydrometers.

Messrs. Thermal Syndicate, Ltd., Neptune Bank, Wallsend-on Tyne.—Tubes, crucibles, basins, artistic dishes, lamp and gas chimneys of fused silica.

Messrs. British Glass Wool Co., 2, Compton Road, London, N.—Samples of glass wool in bulk and in skein.

Messrs. Lang and Son, Charlton Works, Islington, London, N.—Glass tubing and tubes of different sizes, flasks, beakers, burrettes, bottles, surgical appliances, and porcelain basins.

Messrs. Silica Syndicate, 82, Hatton Garden, London, E.C.—Pure fused quartz flasks, distilling flasks, bottles, tubing, basins, crucibles, and vacuum tubes.

Messrs. Morgan Crucible Co., Ltd., Battersea Works, London, S.W.—Clay muffles, tubes, and plates for electrical heating, pyrometer sheaths, combustion boats and tubes, economisers, and gas mantle supports.

Messrs. Lennox Foundry, Ltd., Glenville Grove, London, S.E.—Tantrion plates, basins, cock plugs, and bars.

Messrs. Haughton's Metallic Packing Co., Ltd., 30, St. Mary-at-Hill, London, E.C.—Ironac dishes and cock plugs.

The exhibition was well attended by persons actually interested in the goods displayed, and satisfaction was expressed by many visitors at the considerable progress made in a very short time by British makers of glass and porcelain ware. All the exhibits received careful examination by visitors.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, March 18, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

THE Bakerian Lecture was delivered by Prof. W. H. BRAGG, F.R.S., on "*X-rays and Crystalline Structures.*"

The new method of examining crystalline structure has already been explained on more than one occasion. The atoms of crystal may be conceived in various ways—as arranged in a series of parallel planes, each capable of reflecting a small fraction of an incident pencil of X rays.

If the spacing of the planes is  $d$ , the wave-length  $\lambda$ , and the angle between the rays and the planes is  $\theta$ , and if the relation  $n\lambda = 2d\sin\theta$  is satisfied, where  $n$  is any integer, then the various reflected pencils are in the same phase and combine to give an obvious reflection of the X rays. If this relation is not satisfied there is no reflection.

The X-ray spectrometer is designed to measure the various values of  $\theta$  at which reflection occurs in a given case. The angle can easily be determined to a minute of arc.

Given  $d$  we can compare the wave-lengths of different X-rays. Given  $\lambda$  we can compare the spacings of various sets of planes of the same or of different crystals. By certain considerations the experiments can be made absolute and not merely comparative. In this way the structures of several simple crystals have already been found, such as rock-salt, diamond, iron pyrites, and so on.

The reflections for various values of  $n$ , the integer in the formula, or as they may be called the spectra of various orders, differ amongst themselves in a surprising way. The intensities in the case of the most important planes in Iceland spar have recently been determined, and give very interesting results. In the case of two pairs of planes the spacing is the same but the arrangement of atoms is different. This gives an opportunity of comparing the effect of arrangement apart from spacing, and

it appears that the *intensity* of the reflection in any order is proportional to the weight of the planes which contribute to that order.

Again, there are three calcite planes for which the arrangement of the atoms is exactly the same, but they differ in their spacings. The relative intensities follow a rule which has already been stated, viz., that the intensity in a reflection at an angle  $\theta$  is inversely proportional to  $\sin^2\theta$ , other things being the same. Rules of this kind are needed if the method is to be used in the examination of more complicated crystals. The physical meanings that may be attached to these rules are of considerable interest.

#### PHYSICAL SOCIETY.

March 12, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER ON "*The Estimation of High Temperatures by the Method of Colour Identity*," by C. C. PATERSON and B. P. DUDDING, was read by the former.

Preliminary experiments are described in which the temperature of incandescent substances is estimated with a very fair accuracy by matching their colour with that of incandescent filament lamps working at appropriate efficiencies. These have previously been calibrated by comparison with a "black body" over a large temperature range. The comparisons are made in the field of a Lummer Brodhun photometer, and the method is shown to give the correct result for the melting-point of platinum.

#### DISCUSSION.

Prof. S. P. THOMPSON thought something must be wrong with the English language when "white" light had to be defined as that radiated by a "black" body. The term "grey" body seemed indefinite. There were many shades of grey, and it would be interesting to know how many bodies were really "grey" according to the precise definition of the authors. He thought that in plotting lumens per watt against temperature it would have accorded better with custom to have plotted temperatures as abscissæ instead of as ordinates.

Mr. A. P. TROTTER thought that if this work had been published before the ordinary optical pyrometer had been introduced the latter might never have appeared. The colour identity method appeared to put optical pyrometry on a different plane. Those who had had anything to do with furnaces—he supposed Tubal Cain was the first—always recognised the relation of colour to temperature. The method especially interested him as being an outcome of an investigation of the Violle standard.

Dr. J. A. HARKER said that the accuracy with which the authors had obtained the melting-point of platinum was very surprising. There seemed no *a priori* grounds for supposing that a black body at the temperature of melting platinum should emit the same colour of radiation. With regard to the "black body" used by the authors, it was extremely difficult to obtain a furnace at these high temperatures without a cloudy atmosphere, but after distilling the impurities out of the carbon—which was the only suitable substance to use—he had found it possible to obtain a high temperature furnace with a perfectly clear atmosphere. With the ordinary optical pyrometer it was impossible, by means of the coloured glass supplied, to get sufficiently perfect monochromatism to give great accuracy. If a strip of platinum be used instead of a wire it is possible to maintain it within a degree or two of its melting point for some time.

Mr. A. CAMPBELL asked how the optical pyrometer was calibrated at high temperatures. In the case of the Violle standard, was it essential actually to melt the standard strip? Would it not be more satisfactory to use a tungsten strip heated up until a small speck of *s.g.*

quartz on it began to melt rather than to melt the strip which was under observation?

Mr. Dow questioned whether the filaments of the lamps could be regarded as "grey" bodies, as, when metal filaments first came out and their energy wave-length curves were taken, these showed large irregularities in the infra-red. Some of the work done in the States with the hot filament type of optical pyrometer showed that interference fringes made it difficult to note the point when the filament was invisible against the background. The authors' method had no disadvantages of this kind on account of the size of field used.

Mr. A. W. BEUTTELL suggested that any difference in the colour sensations of the observer from the normal would affect the results obtained by the method.

Dr. C. CHREE asked which of the values, 1750° C. or 1770° C., the authors considered most nearly correct?

Mr. E. H. RAYNER thought it might add to the sensitiveness of the method if, when the colour match had been obtained, coloured glasses—say, first a red and then a blue glass—were put in front of the eye. Any inexactness in the match might be increased and shown up in this way.

Mr. PATERSON, in reply, said that the terms "black" and "grey," as applied to radiating substances, were widely used and had quite definite meanings. The grey bodies quoted by Prof. Thompson should really be classed as selective. There were very few substances, of course, which were absolutely "grey," and it was well to consider everybody as having a large amount of greyness and a small amount of selectiveness. With regard to Mr. Dow's remarks, all bodies were almost entirely grey within the visible spectrum. It was chiefly outside these limits that irregularities occurred. Peculiarities in colour sensation could not affect the result, as the radiation from both sources was similarly affected. "Black body" temperatures were, he believed, obtained where possible by means of thermocouples, and at higher temperatures the curve was extrapolated by means of the radiation laws. He regarded the values 1750 and 1770 as agreeing within the limits of accuracy of these preliminary experiments.

A paper on "*The Unit of Candle-power in White Light*," by C. C. PATERSON and B. P. DUDDING, was read by the latter.

The paper describes the methods adopted at the National Physical Laboratory for minimising the difficulty of photometric comparison of white lights of different hue. A series of six sets of electric sub-standards are described, varying in the tint of the light radiated from that of the pentane lamp to that of a tungsten vacuum lamp operating at 1.5 watts per candle. The absolute value of the unit of candle power has been re-determined, as have also the corrections for humidity and barometric changes, while the probable existence of a temperature correction is discussed.

#### DISCUSSION.

Mr. A. P. TROTTER said he would only refer to the question of the humidity correction. Considerable work had been done by Messrs. Haldane and Butterworth and himself, which had not yet been published, in which observations had been taken over larger ranges of humidity than in the American observations. The barometer was also varied over a wide range. The curve they obtained had a tangent which accurately fitted in with the authors' observations. The suggestion that a temperature correction lurked within the humidity coefficient was possible. The intensity-moisture curve was a sloping straight line which might be the resultant of two lines—the true moisture-intensity line of slightly greater slope than the observed curve combined with a temperature-intensity curve of small negative slope.

Mr. Dow thought that the cascade method did not get over any fundamental difficulty inherent in the direct comparison of the differently hued lights, and he was inclined to question whether the increased accuracy attained, if



any, in the final result really warranted the additional trouble. It was well known that the colour depended on the area of the retina illuminated, and he asked if the authors had found that any difference could be produced by pushing in or drawing out the draw tube of the photometer. He asked what was the degree of reproducibility of the pentane standard. He noted that the authors did not like flicker photometers. His experience agreed with this.

Mr. A. CAMPBELL also thought that the figures in the paper did not justify the conclusion that the cascade method was much superior to the direct comparison of the sources.

Mr. T. SMITH (communicated remarks) thought it would be of interest to have a curve showing the results obtained for lamp 6 directly compared with each of the intermediate sub-standards. He suggested that the difficulty experienced in photometry involving a colour difference might be due to the chromatic aberration of the eye preventing both portions of the contrast pattern being in simultaneous focus. If numerical data concerning this aberration were available a lens could be computed which would allow simultaneous focus for the different colours, and might in great part remove the difficulty.

Mr. PATERSON, in reply, said that Mr. Trotter's suggested explanation of the temperature coefficient was similar to the one they had themselves formed. A given range of temperature in America might be accompanied by a different variation in humidity than the same range of temperature here. Using the cascade method all observers agreed very closely, and while it appeared to give the same ultimate result as direct comparison, this could not have been taken for granted beforehand. With large colour differences the judgment of an observer seemed to vary more from time to time than when bridging the difference in small steps. He did not think that the pentane standard could be reproduced more closely than about 1 per cent, but they had always used one particular lamp as their ultimate standard at the National Physical Laboratory.

A paper, entitled "*The Relative Losses in Dielectrics in Equivalent Electric Fields, Steady and Alternating (R.M.S.).*" by Mr. G. L. ADDENBROOKE, was taken as read on account of the lateness of the hour.

After references to former work, especially on surface leakage, tables are given showing an intimate connection between the losses in steady and alternating fields, and that the one can be predicted from the other to a first approximation. Exceptions are mentioned, and it is shown that there is heterogeneity in these cases. Curves of the losses from 1 to 4 seconds to 40 vibrations are given for specimen dielectrics. Above 8 to 12 vibrations, both for "good" and "poor" dielectrics, these become rising straight lines. The salient features lie below, about 16 vibrations.

The formula  $a + bn$  applies to all dielectrics for frequencies above about 8 vibrations, but not below. The  $a$  constant is always larger than and bears only a very indefinite relation to the steady voltage loss. Liquid dielectrics behave similarly to solid with certain differences, particularly that for a given resistance the ratio of the steady to the alternating loss is less than with solids. There is a great difference in the comparative ranges of the losses. For the dielectrics tabulated these vary in a steady field from 1 to 1,300,000, but the corresponding alternating losses vary only from 1 to 1100. The difference is principally in the "good" dielectrics, the alternating losses in which at 40 vibrations are vastly larger than these in a steady field, though they still appear to be connected with them.

#### DISCUSSION.

Mr. D. OWEN (communicated remarks) considered that the author's tests supplied data of great interest, though their value would be greater if more details of actual readings were supplied. The results support the  $a + bn$

formula for dielectric power loss already advanced by previous workers. They show also that  $a$  and  $b$  are probably unconnected. This being the case, the author has adopted a wrong basis of calculation in arriving at his main point. It would be better to show the relation between  $a$  and  $a_0$ , the direct current power loss. The discrepancies noted in regard to a few materials (good insulators) might thus be found to disappear.

## NOTICES OF BOOKS.

*Practical Physical Chemistry* By ALEX. FINDLAY, M.A., Ph.D., D.Sc. Third Edition. London, New York, Bombay, Calcutta, Madras: Longmans, Green, and Co. 1914.

IN the third edition of this book its limits have been very considerably extended, fresh subjects and new methods of work having been added to make it a more complete laboratory book of physical chemistry. In its present form it contains all that the average general student of chemistry requires, and it provides an excellent introductory course for the use of those who intend to specialise in the subject. The descriptions of typical methods and experiments are very clear, and for the benefit of more advanced students many references to original literature have been added to the third edition.

*The Chemistry of Colloids and some Technical Applications.* By W. W. TAYLOR, M.A., D.Sc. London: Edward Arnold. 1915.

THIS book is based upon a series of lectures delivered by the author to the advanced students of the University of Edinburgh, and is the first general text-book on the subject which has been published in the English language. In the first part the general properties of colloids are treated, the author's plan being first to describe the phenomena and then to discuss the most important explanations and theories which have been put forward. The student is supposed to have a reasonable knowledge of mathematics, and if that is the case he should have no difficulty in following the text, in which the arguments are always lucidly stated. In the second part the practical details of methods of preparation of sols are given, and Part III. deals with adsorption. Some account of the applications of colloid chemistry, e.g., in dyeing, tanning, and biology, is given in the last section, the first subject being discussed in some detail, although the author does not claim to have treated it by any means completely or exhaustively.

## OBITUARY.

DR. S. G. RAWSON.

It is with great regret that we have to record the death of Dr. S. G. Rawson, the Principal of the Battersea Polytechnic, who died, after a brief illness, on Tuesday, March 23.

Dr. Rawson was educated at Charterhouse School, the Royal College of Science, University College, London, University College, Liverpool. He subsequently became Lecturer in Chemistry at University College, Liverpool, and in 1895 he was appointed Principal of the Technical College, Huddersfield. In 1903 he was appointed Director of Education to the Worcestershire County Council, and in September, 1907, he was appointed Principal of the Battersea Polytechnic.

Dr. Rawson was a Doctor of Science of the University of London, an Associate of the Royal College of Science, Liverpool, Fellow of the Institute of Chemistry and of the Chemical Society, and, since January, 1914, was Chairman of the Council of the Association of Technical Institutions.

A memorial service to the late Dr. Rawson was conducted at the Polytechnic by the Rev. Canon Curtis, Chairman of the Governing Body, on Friday morning, March 26. The Great Hall of the Polytechnic, which was appropriately draped for the occasion, was crowded with members of the staff and with students of the various departments of the Polytechnic, assembled to pay the last tribute of respect and affection to their late Principal. The service, which was fully choral, was most impressive and affecting. In addition to the staff and students, the service was attended by members of the Governing Body, Sir Philip Magnus, of the City and Guilds Institute, Mr. Edwin Tate (formerly Chairman of the Governing Body), Mr. E. an Spicer (a former Governor), Dr. Garnett, and other representatives of the Education Department of the London County Council, the Principals of most of the London polytechnics, and representatives of other bodies with which the late Dr. Rawson was connected.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cix., No. 7, February 15, 1915.

This number contains no chemical matter.

No. 8, February 22, 1915.

**Favourable Action of Manganese on the Bacteria of Leguminous Plants.**—D. OLAVU. —It has been shown that manganese, traces of which are found in all living cells and in all soils, has a beneficial effect upon crops when small quantities of soluble salts are added to soils deficient in it. The author has studied the influence of manganese upon the microbes of the soil, beginning with those of the nodosities of leguminous plants, and has found that it has a favourable effect upon the bacteria which cause the fixation of nitrogen.

## MISCELLANEOUS.

**Methods of Analysing Sulphur.**—M. G. LEVI.—Carius' method of determining sulphur is not very accurate, being affected by a small positive error. Oxidation in a current of oxygen provides an accurate and easy method of estimation, if the specimen is fairly pure, but is not satisfactory if appreciable quantities of bitumen are present. The two best processes are oxidation with nitric acid and bromine, performed according to the author's directions, and Fresenius's method.—*Annali di Chimica Applicata*, I., 1915, p. 9.

**Determination of Free or Combined Glycerin. Application to Glycerophosphates.**—M. FRANÇOIS and E. BOISMENU.—Free glycerin, after having been deprived of all volatile substances such as alcohol and water, can be recognised by the following reactions.—Transformation into acrolein by heating with potassium bisulphate, red coloration produced with acrolein and bisulphited rosaniline, transformation of red coloration into blue

coloration by heat. The combined glycerin of glycerophosphates can be characterised by the same method, and probably also that of lecithins. The oxidation of free glycerin by chromic mixture gives carbon dioxide and water only if a large excess of potassium bichromate is employed, concentrated sulphuric acid is used and boiling is continued long enough. In this case oxidation is complete, otherwise it is incomplete. Henner's and Martin's methods of determining glycerin are accurate only if these conditions are fulfilled. After treating with chromic mixture the phosphorus of glycerophosphates can be determined as magnesium pyrophosphate, and probably the phosphorus of lecithins can be estimated similarly.—*Journal de Pharmacie et de Chimie*, 1915, xi., No. 2.

**Royal Institution.**—The Day Lectures after Easter:—Banister Fletcher, three lectures, "The War on Architecture"—(1) The War on French Architecture; (2) The War on Rheims Architecture; (3) The War on Belgian Architecture." Prof. Charles S. Sherrington, two lectures, "The Animal Spirits." Prof. Frederick Soddy, two lectures, "Advances in the Study of Radio-active Bodies." Prof. J. O. Arnold, two lectures, "The Evolution of Steel Influence on Civilisation." Prof. A. S. Eddington, two lectures, "The System of the Stars"—(1) Star Colour and its Significance; (2) The Stellar System in Motion." Dr. A. W. Porter, two lectures, "Advances in General Physics." Prof. V. H. Blackman, two lectures, "The Movements and Activities of Plants." Wilfrid Ward, three lectures, "Method of Presenting Character in Biography and Fiction." Lieut. Col. A. G. Hadcock, two lectures, "Modern Artillery." Prof. J. A. Fleming, two lectures, "Photo electricity" (the Tyndall Lectures). Dr. Martin O. Forster, two lectures, "Colouring Matters of the Organic World"—(1) Colouring Matters of Nature; (2) Dyes, the Creation of the Chemist." Prof. Robert S. Rait, three lectures, "Mary Queen of Scots"—(1 and 2) Mary Stuart and Elizabeth; (3) Mary Stuart and her Son." The Friday Evening Discourses will begin on April 16. Mr. Stephen Graham, "The Russian Idea"; Major P. S. Lelean, "Military Hygiene at the War"; followed by Canon Pearce, Sir John Jackson, Sir Ernest Rutherford, Dr. H. Walford Davies, Profs. F. G. Dunnan and O. W. Richardson, and Edward Heron-Allen.

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# THE CHEMICAL NEWS.

VOL. CXI., No. 2889.

## THE NITROGEN OF PROCESSED FERTILISERS.\*

By ELBERT C LATHROP,  
Scientist in Soil Fertility Investigations.

(Continued from p. 164).

**Monoamino Acids.**—Although leucine and tyrosine, which are protein decomposition products, were found in about the same quantities, the methods of isolation were so far from being quantitative that this relationship is of no significance. The isolation and identification of the other monoamino acids from the complex products of protein hydrolysis can only be accomplished in the majority of cases by means of the esterification method of Emil Fischer. This method is not a strictly quantitative one, and requires large amounts of materials for a successful separation, and consequently was not used in this investigation. The use of methods other than that of esterification failed to isolate any other monoamino acid in quantities large enough for identification. As will be shown later, a number of monoamino acids besides the two isolated must be present in the processed goods.

Establishing the presence of these products of acid hydrolysis of proteins, namely, the diamino acids, arginine, lysine, and histidine, and the two monoamino acids, leucine and tyrosine, in the amounts in which they were found, is of itself sufficient evidence to demonstrate that by the acid treatment of the crude materials used in the manufacture of the base goods the proteins contained therein have been changed. This change is shown to be a deep-seated one, since five of the compounds which are known to be final products of protein hydrolysis by acids are found. This, however, can not be taken to mean that the proteins have been completely hydrolysed by the acid treatment, since it is possible to have present in the product of partial hydrolysis of proteins not only the diamino and monoamino acids, but also such intermediate compounds as polypeptide, peptones, proteoses, &c.

In this connection the results obtained by use of the Van Slyke method, which are given in Table V., are of particular interest. As has been already stated, the base goods were extracted (1) with boiling water and (2) with boiling acid. In the former case, only slight further hydrolysis of the materials in the base goods is to be expected, since the free acid in the fertiliser is extremely weak, and the boiling temperature, 100° C., is that which was reached in the process of manufacture. In the case of the second extract, complete hydrolysis of all the proteins or protein-like materials is certainly to be expected, since in addition to the original hydrolysis the material was boiled with strong hydrochloric acid for twenty-four hours, which treatment in the case of most proteins is sufficient for complete hydrolysis. The differences in the results obtained from the analyses of the two extracts may, therefore, be expected to throw some light on the question of the completeness of hydrolysis of the original proteins by the acid processing.

First, it will be noticed that total soluble nitrogen in the hydrochloric acid extract is 88.64 per cent of the total N, while that of the water extract is 85.24 per cent, showing a difference of 3.4 per cent soluble N produced by further hydrolysis of the materials in the base goods. Correspondingly there is a decrease of insoluble N. There is an increase of 0.47 per cent amide N in the hydrochloric acid extract over that in the water extract. This is due to

the splitting off of ammonia from some nitrogenous compounds by the hydrochloric acid, and suggests the presence of some product of partial protein hydrolysis in the fertiliser which contains an acid amide linkage.

TABLE V.—Nitrogen forms as determined by the Van Slyke method.

Form of nitrogen.	Results expressed in per cent of base goods.		Results expressed in per cent of total N in base goods.	
	H <sub>2</sub> O extract.	HCl extract.	H <sub>2</sub> O extract.	HCl extract.
Total N .. ..	1.610	1.610	—	—
Total soluble N	1.372 (a)	1.435	85.24 (a)	88.64
Total insoluble N	0.238 (a)	0.175 (a)	14.76 (a)	11.36 (a)
Amide N .. ..	0.374	0.382	23.23	23.70
Humin N .. ..	0.091	0.074	1.95	4.61
Diamino acid fraction—				
Arginine N ..	0.111	0.104	6.89	6.46
Histidine N ..	0.117	0.070	7.26	4.38
Lysine N ..	0.081	0.117	5.06	7.26
Monoamino acid fraction—				
Amino N ..	0.543	0.546	33.75	33.92
Nonamino N ..	0.114	0.133	7.10	8.27

(a) Obtained indirectly.

The statement has already been made that nitrogenous compounds other than arginine, histidine, and lysine are included under the figures given for these compounds in the table. This is due to the fact that the phosphotungstic acid, which is used as a precipitant of the diamino acids, also precipitates peptones, proteoses, &c., as well as the purine bases, cystine, and possibly other compounds. Since nitrogen compounds other than proteins existing in the original material, and susceptible to decomposition with hot acid, would have been already broken up in the processing, it follows that the changes produced by further boiling with acid would result from peptones, proteoses, &c. The difference noted between the results obtained from the two extracts for the diamino acids are therefore due to some interfering substances of the nature of proteins and not to such substances as the purines or cystine. Moreover, the latter compounds will produce the same relative error in analysis in the case of both extracts.

Of the diamino acids the only one determined directly is arginine. Its determination depends on the fact that when arginine is boiled for some time with strong potassium hydroxide, half of the nitrogen of the arginine is split off as ammonia. However, if cystine is present 28 per cent of its nitrogen is evolved as ammonia, together with the arginine nitrogen. As has already been stated, this figure should be the same for the two extracts providing that there is present in the base goods no substance precipitated by phosphotungstic acid, and giving off ammonia when boiled with strong alkali or strong hydrochloric acid. A comparison of the results obtained for arginine in the two extracts shows that the figure for arginine in the water extract is higher than that of the hydrochloric acid extract by 0.43. In other words, there appear to be present in the diamino acid fraction compounds which on boiling with alkali give off ammonia amounting to 0.22 per cent of the total nitrogen. These compounds are broken up by the further hydrolysis with acid.

Further information may be obtained by a consideration of the figures for lysine and histidine, which are obtained not by a direct determination but by calculation from the figures obtained for arginine N, total N in the fraction, amino N, and non-amino N. Lysine contains only amino N, histidine contains one-third amino N and two-thirds non-amino N, while arginine contains one-fourth amino N and three-fourths non-amino N. Since histidine N is in a measure obtained by difference from the non-amino N and the arginine N, according to formula (1) (see ante), it is evident that if there are precipitated by the phosphotungstic acid compounds which contain non-amino N

\* Bulletin No. 158, United States Department of Agriculture, Bureau of Soils.

other than arginine and histidine, such nitrogen will be classed as histidine N, because the arginine N is determined directly.

A comparison of the results for histidine shows that there is 2.88 per cent less N calculated as histidine in the hydrochloric acid extract than in the water extract, and at the same time there is an increase in lysine N in the hydrochloric acid extract amounting to 2.20 per cent. This shows that by the hydrolysis with hydrochloric acid some substance which reacted as though it contained non-amino N has been decomposed, with the formation of an almost corresponding amount of amino N. Here again the indications are that this substance is of the class of compounds related to the proteins.

This is further borne out by the fact that in the mono-amino acid fraction the nitrogen listed as amino N has increased in per cent 0.17 and the nitrogen as non-amino N has increased in per cent 1.17 by hydrolysis with hydrochloric acid.

A comparison of the figures for humin N shows an increase of 2.66 in the hydrochloric acid extract, but since the nature of the compounds in which this class of nitrogen exists is not understood no interpretation can be given to this figure.

**Proteoses.**—In order to prove the presence of some intermediate product of protein hydrolysis, which is thus indicated by analytical methods, an aqueous solution of about 2.5 pounds of base goods was made, and the di-amino acids were precipitated with phosphotungstic acid in the presence of 5 per cent sulphuric acid. The precipitate which formed was allowed to stand over night, and after filtering off it was washed well with 5 per cent sulphuric acid. The precipitate was dissolved in sodium hydroxide, the phosphotungstic acid precipitate by adding barium hydroxide solution, and after filtering the excess of barium was removed by adding sulphuric acid until a neutral reaction was obtained. Portions of this solution were tested for peptones, proteoses, &c., with the following results:—The biuret test was positive; a precipitate was obtained on saturation of the solution with ammonium sulphate or with sodium chloride; when the filtrate from the latter solution was treated with acetic acid a cloudy precipitate developed. Precipitates were also obtained with sulphuric acid, hydrochloric acid, phosphomolybdic acid, and with phosphotungstic acid. A precipitate was formed on the addition of alcohol to the solution. This precipitate was filtered off, dissolved in dilute alkali, and on addition of very dilute copper sulphate solution the biuret reaction was again obtained. These reactions are those which are given by proteoses and by the proteins, and confirm the conclusions arrived at from the results obtained with the Van Slyke method. The Millon reaction and the Hopkins-Cole reaction were both negative, showing the absence from this protein-like compound of the tyrosine and the tryptophane radicles.

A very large number of compounds intermediary between the protein and its primary hydrolysis products may occur, depending on a great variety of conditions, so that the actual identification of the compound under discussion would be a difficult matter. However, the nature of this compound may be approximately determined by the results obtained in the study of the two extracts by the Van Slyke method. These results have been already discussed, and they indicate the presence in the base goods of a compound of a proteose nature, which because it gives a biuret test must be composed of at least three amino acids. The results indicate still further that the compound is composed of acid amide radicles, diamino acids, particularly lysine and monoamino acids, those containing amino nitrogen, and especially those containing non-amino nitrogen. Since the figures obtained by the nitrogen partition method are subject to a certain amount of error when applied to such a mixture, the figures can only be taken as approximate for the various forms of nitrogen which make up this compound.

The figures given for arginine in the table are probably

only influenced by any cystine present. Attempts to isolate cystine from the base goods failed, although it seems unlikely that this compound can be absent. The figures for histidine and lysine are undoubtedly too high, since they include all of the other nitrogenous compounds precipitated by phosphotungstic acid, so that the absolute amount of these compounds in base goods can not be correctly determined by this method. The figure given for the amount of amino nitrogen present as monoamino acids may be a little high, while the non-amino nitrogen figure is open to considerable error.

In Table VI. are given the primary hydrolysis products of a number of proteins which may be present in the base goods. These results were obtained by the esterification method, and show how the different proteins vary in the nature and amount of the units composing them. Many monoamino acids besides leucine and tyrosine occur in these proteins, and there must consequently be present in the base goods amino acids other than the two isolated. This is apparent from the composition of the various proteins shown in the table. Owing to the large amount of amide nitrogen present in the fertiliser, which was split off by the acidulation of the original proteins of the trade wastes, it may be concluded that considerable quantities of aspartic or glutamic acids are present in this sample of base goods.

The conclusions which are to be drawn from the results obtained by the examination of this fertiliser by means of the analytical and isolation methods are as follows:—The process by which the nitrogen of certain trade wastes—such as hair, leather, garbage, &c.—is made more available is recognised as a process of partial hydrolysis of the complex protein contained in such materials, resulting in ammonia, amino acids, &c., all of which are more available than the original protein material. This hydrolysis is almost complete, the nitrogenous compounds formed being principally the primary products of protein hydrolysis, together with a small amount of proteose-like compound which has not been fully decomposed.

#### *Availability of the Nitrogen of Organic Fertilisers.*

The question of the availability of the different kinds of nitrogen contained in organic fertilisers is one that has caused considerable discussion. A number of methods have been proposed for determining this factor, and while some of them give helpful results, all excepting the plant method are open to more or less objection. The reason for this is that the methods are empirical and the nature of the complicated compounds in which the nitrogen is linked in the fertiliser is unknown or only guessed. When these nitrogen compounds are known, and their action on plants as well as the action of the compounds which will be formed from them during their decomposition in the soil has been determined, then the question of the availability of the nitrogen of organic fertilisers can be understood. Originally it was held that plants were only able to use nitrogen when it was offered to them in the form of nitrates; this idea, however, was modified when it was discovered that under certain conditions plants used ammonia or ammonium salts without their conversion into nitrates quite as well as they used the nitrates themselves. During the past few years it has been clearly demonstrated that plants not only use nitrogen in the form of nitrates and ammonia, but that they can also use nitrogen in the form of complex organic compounds (Hutchinson and Miller, *Centralb. j. Bakt.*, 1911, xxx., 513; Schreiner and Skinner, 1912, *Bul.* 87, Bureau of Soils, U.S. Dept. Agr.). The action of a number of these nitrogenous compounds has been tested in this laboratory in conjunction with the three fertiliser elements, and it has been found that in some cases the nitrogen compounds are not only used as a source of nitrogen for the growing plant, without any change in the compound, but that these compounds were apparently nitrate spacers; that is, the plant used them in preference to the nitrates. Instead, then, of only one kind of nitrogen compound, nitrate, or at most two,

TABLE VI.—Products of Acid Hydrolysis of various Proteins.

Compound.	"Synotin" from cattle flesh. (a)	"Keratin" from sheep's horn. (b)	"Keratin" from sheep's wool. (c)	"Keratin" from horse's hair. (d)	Halibut muscle. (e)	Ox muscle. (f)	"Legumin" from pea (g)
Glycine (h) . . . .	0.5	0.5	0.6	4.7	0.0	2.1	0.4
Alanine (h) . . . .	4.0	1.6	4.4	1.5	(?)	3.7	2.1
Valine . . . . .	0.9	4.5	2.8	0.9	0.8	0.8	—
Leucine (h) . . . .	7.8	15.3	11.5	7.1	10.4	11.7	8.0
Isoleucine . . . . .							
Phenylalanine (h) . .	2.5	1.9	—	0.0	3.1	3.2	3.8
Tyrosine (h) . . . .	2.2	3.6	2.9	3.2	2.4	2.2	1.6
Serine . . . . .	—	1.1	0.1	0.6	(?)	(?)	0.5
Cystine . . . . .	—	7.5	7.3	8.0	—	—	—
Proline . . . . .	3.3	3.7	4.4	3.4	3.2	5.8	3.2
Oxyproline . . . . .	—	—	—	—	—	—	—
Aspartic acid (h) . .	0.5	2.5	2.3	0.3	2.8	4.52	5.3
Glutamic acid (h) . .	13.6	17.2	12.9	3.7	10.1	15.5	17.0
Tryptophane . . . .	—	—	—	—	(+)	(+)	(+)
Arginine (h) . . . .	5.1	2.7	—	4.5	6.4	7.5	11.7
Lysine (h) . . . . .	3.3	0.2	—	1.1	7.3	7.6	5.0
Histidine (h) . . . .	2.7	—	—	0.6	2.6	1.8	1.7
Ammonia (h) . . . .	0.9	—	—	—	1.4	1.1	2.1
Total . . . . .	47.3	62.3	49.2	39.6	50.7	67.5	62.4

(a) E. Abderhalden and T. Sasaki (*Zeit. Phys. Chem.*, 1907, li., 404).

(a), (b), (c) E. Abderhalden and A. Voitinovici (*Zeit. Phys. Chem.*, 1907, lii., 348).

(d) E. Abderhalden and H. G. Wells (*Zeit. Phys. Chem.*, 1905, xli., 31); A. Argiris (*Ibid.*, 1905, liv., 86).

(e) T. B. Osborne and F. W. Heyl (*Am. Journ. Phys.*, 1908, xxii., 433).

(f) T. B. Osborne and D. B. Jones (*Am. Journ. Phys.*, 1909, xxiv., 437).

(g) T. B. Osborne and F. W. Heyl (*Journ. Biol. Chem.*, 1908, v., 197).

(h) Physiological action on plant growth has been determined and reported in *Bull. 87*, Bureau of Soils, U.S. Dept. Agr.

nitrate and ammonia, there appears to be a very large number of nitrogenous compounds which have properties of physiological importance to plant growth. The question of the availability of nitrogen compounds can therefore be answered only when the nitrogen compounds contained in the fertiliser can be determined in amount and at the same time classified according to their physiological action on plant growth. It is hardly necessary to state that such a method does not exist at present, and that the physiological action of only a part of the total number of nitrogenous compounds present in fertilisers is known.

The physiological action on plants of all of the nitrogenous compounds isolated from base goods has been determined by means of water cultures (*Bul. 87*, Bureau of Soils), and the results obtained may be stated briefly as follows:—Both of the purine bases are used by the plant as a source of nitrogen, and are beneficial to plant growth; furthermore, the hypoxanthine acts as a nitrate sparer, there being less nitrate used by the plant in the presence of hypoxanthine than when the hypoxanthine is absent. Histidine, arginine, and lysine (unpublished data) are all beneficial to plant growth, causing nitrogen increases in the plant, and the two first diamino acids act as nitrate spacers; this may also be true of lysine, although this property of lysine has not been studied. Leucine is also beneficial to plant growth, and tyrosine in the light of later investigations is somewhat doubtful in action. Of the other monoamino acids which may be present in base goods, aspartic acid, glutamic acid, and glycocholl have been found to be beneficial. The action of alanine is somewhat doubtful, it apparently being beneficial in low concentrations, and the action of phenylalanine is reported as harmful. Thus we see that six of the seven compounds isolated from the base goods are actually available to plants as such, and have a beneficial action. Of the monoamino acids, other than the two isolated from base goods, which have been studied in regard to their action on plant growth, three have been found to be beneficial, one doubtful, and one is reported as being harmful.

The high-grade nitrogenous fertilisers, such as dried blood, are considered to have a high availability owing to the fact that the nitrogenous materials when placed in the soil quickly undergo the process of ammonification and nitrification, the nitrogen thus being changed into a form which can be immediately used by the plant. In fact, Lipman (*Bul. 246*, 1912, New Jersey Expt. Sta.) has proposed a method for the determination of the availability of the nitrogen of organic fertilisers, depending on the amount of ammonia produced under certain conditions in a given length of time. It is evident from the above consideration that such a method does not tell the whole story, since in the decomposition of protein materials like dried blood intermediate compounds are formed which are undoubtedly in themselves beneficial to plant growth. In order, therefore, to understand the complete action of the nitrogenous materials in the base goods it is necessary to know how the compounds contained in it are acted upon by ammonifying bacteria. Jodidi (*Research Bul. No. 9*, Iowa Expt. Sta.) has shown that the amino acids and acid amides are quite readily ammonified when placed in the soil, the rate of ammonia formation and the amount of ammonia formed depending apparently upon the chemical structure of the particular compound under consideration. In general he found that the simpler the chemical structure of the nitrogen compound the more quickly and readily it was ammonified. In the light of these facts it appears that polypeptids, peptones, proteoses, and proteins would be ammonified still more slowly than the amino acids, since their structure is increasingly more complex.

Hartwell and Pember (*loc. cit.*), in their study on the availability of the nitrogen of base goods, by means of plant tests found that it had apparently as high an availability as dried blood; the water soluble nitrogen having even a higher availability. From the nature and amounts of the compounds present in the base goods this might be predicted. In the case of the dried blood the nitrogen is practically all in the form of complex protein material, which must be broken down into simpler compounds by bacterial action, with the formation of ammonia and other



nitrogenous compounds, some or all of which may be of physiological importance to plants. With the base goods the case is a little different. The greater part of the nitrogen is at once available for plant use, and at the same time these available compounds may be changed more easily and quickly by the bacteria of the soil into ammonia and nitrate, which in turn are used by the plant. The soluble nitrogen of base goods should, therefore, be in a more readily available form than the nitrogen of dried blood or other nitrogenous fertilisers which are entirely of a protein nature.

(To be continued).

### THE SEPARATION AND ESTIMATION OF ALUMINIUM ASSOCIATED WITH IRON, BY THE ACTION OF ACETYL CHLORIDE IN ACETONE.

By H. D. MINNIG.

WATER becomes so modified as a solvent for barium chloride when hydrogen chloride is dissolved in it to saturation that this salt, which is easily soluble in pure water, dissolves in the saturated aqueous hydrochloric acid only in the proportion of 1 to about 20,000 parts. The addition of ethyl ether to the concentrated aqueous hydrochloric acid thus produced so diminishes the solvent action of the mixture upon barium chloride that the salt will then dissolve in the proportion of 1 to about 120,000 parts. Barium chloride may therefore be separated with accuracy from the ether-hydrochloric acid solution of the chlorides of calcium and magnesium which remain soluble in high degree, as was shown in a former paper from the Kent Chemical Laboratory of Yale University (Mar, *Am. Journ. Sci.*, 1892, [3], xliii., 521).

Aluminium chloride, as was subsequently shown (Gooch and Havens, *Am. Journ. Sci.*, 1896, [4], ii., 416), may be similarly precipitated by thorough saturation of the cooled aqueous solution after addition of an equal volume of ether, and effectively separated from iron, and by the same procedure aluminium may be separated from beryllium, zinc, copper, mercury, and bismuth (Havens, *Am. Journ. Sci.*, 1897, [4], iv., 111; 1898, vi., 45).

Instead of charging the water solution with gaseous hydrogen chloride that reagent may be produced by the action of acetyl chloride upon the water, and this reaction has been tested more recently in its application to the precipitation of barium chloride (Gooch and Boynton, *Am. Journ. Sci.*, 1911, [4], xxxi., 212)—inconvenient violence of reaction being moderated by acetone, which mixes in all proportions with both acetyl chloride and water, and by itself exerts no appreciable solvent action upon hydrous barium chloride.

The present paper is the account of results obtained in applying the acetone acetyl chloride mixture to the precipitation of aluminium as chloride, and the separation of that element from iron. In preliminary experiments it was found that the hydrous aluminium chloride,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , may be precipitated completely by the [4:1] acetone-acetyl chloride mixture, and after careful drying may be converted directly to the oxide by ignition. In the quantitative experiments recorded below the aluminium chloride, prepared by saturating a strong solution of the commercial salt with gaseous hydrogen chloride and washing with concentrated hydrochloric acid until free from iron, was dissolved in water, and the solution was standardised by precipitating the aluminium hydroxide, igniting, and weighing the oxide. The acetone-acetyl chloride mixture was made up in the proportion of four of acetone to one of acetyl chloride. In each experiment a portion of the standard solution was measured from a pipette into a small beaker, and evaporated on the steam-bath to the smallest possible volume. To the concentrated solution, cooled by immersing the beaker in

running water at a temperature of about  $15^\circ$ , or in ice-water, the acetone-acetyl chloride mixture was added drop by drop, with stirring, to the amount of 15 cc. to 20 cc. The precipitate was transferred to a perforated crucible, washed with the precipitating mixture, dried for ten or fifteen minutes high above a low Bunsen flame, which was gradually increased to its fullest heat. Covering the precipitate with red mercuric oxide (to prevent mechanical loss during the ignition), and igniting under a good draft-hood was tried in a few cases, but without advantage over the simpler method. The results of experiments made with the pure aluminium chloride are given in Table I.

In Table II. are given the results obtained by similar procedure in the precipitation of the aluminium chloride from solutions containing also known amounts of ferric chloride.

TABLE I.

Solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ taken.	$\text{Al}_2\text{O}_3$ by standard. Grm.	$\text{Fe}_2\text{O}_3$ used, present as chloride. Grm.	$\text{Al}_2\text{O}_3$ found. Grm.	Error. Grm.
5	0.0213	—	0.0213	—
5	0.0213	—	0.0212	-0.0001
5	0.0213	—	0.0213	—
5	0.0213	—	0.0214	+0.0001
5	0.0213	—	0.0215	+0.0002
10	0.0426	—	0.0426	—

TABLE II.

5	0.0213	0.0293	0.0215	+0.0002
5	0.0213	0.0293	0.0211	-0.0002
5	0.0213	0.0293	0.0213	—
5	0.0223	0.0293	0.0212	-0.0001
5	0.0213	0.0293	0.0213	—
5	0.0213	0.0293	0.0214	+0.0001
10	0.0426	0.0293	0.0426	—
10	0.0426	0.0586	0.0425	-0.0001

TABLE III.

15	0.0592	0.0373	0.0597	+0.0005
15	0.0592	0.0373	0.0602	+0.0010
15	0.0592	0.0746	0.0600	+0.0008
15	0.0592	0.0746	0.0602	+0.0010
15	0.0592	0.0373	0.0603	+0.0011
15	0.0592	0.0373	0.0606	+0.0014

TABLE IV.

1.	15	0.1661	0.0373	0.1662	+0.0001
2.	15	0.1661	0.0746	0.1666	+0.0005
3.	15	0.1661	0.1492	0.1661	—
4.	30	0.1854	0.0746	0.1852	-0.0002
5.	30	0.1854	0.1119	0.1860	+0.0006
6.	30	0.1854	0.1865	0.1862	+0.0008
7.	30	0.1854	0.1865	0.1856	+0.0002
8.	30	0.1854	0.3730	0.1856	+0.0002
9. (a)	30	0.1854	0.2611	0.1856	+0.0002
10. (a)	30	0.1854	0.3730	0.1839	-0.0015
11.	45	0.2781	0.0746	0.2779	-0.0002
12.	45	0.2781	0.0746	0.2787	+0.0006

(a) After decanting the acetone acetyl chloride solution of iron through the filter and washing the precipitate of the hydrous aluminium chloride with the precipitating mixture to remove as much of the iron as possible, the precipitate in the beaker was dissolved in the smallest possible quantity of water, and re-precipitated by the acetone-acetyl chloride mixture. There is great danger of mechanical loss due to the creeping tendency of the ferric chloride in acetone-acetyl chloride solution, and the separation is sharp enough to obviate any necessity of the second precipitation to avoid danger of inclusion of the iron.

In the experiments of Table II. the iron was precipitated by  $\text{NH}_4\text{OH}$  after cautiously diluting the filtrate with water, and then determined gravimetrically as the oxide. The error of the results ranged from +0.0004 grm. to +0.0013 grm. in terms of ferric oxide. On investigation this was found to be due to ferric phosphate derived from the phosphorous compounds used in the preparation of the acetyl chloride.

Since the precipitation of the aluminium was quantitative and rapid, and iron could be determined easily other than as the oxide, larger quantities of aluminium were used with measured quantities of ferric chloride without determining the iron in the filtrate. With the use of larger quantities of the acetone-acetyl chloride solution necessary for the increased amount of the salts, the aluminium chloride precipitate also began to include phosphate appreciably, as is shown in Table III.

Many efforts were made to purify the contaminated acetyl chloride, by redistilling after refluxing (for six or seven hours) with a return condenser over sodium acetate (Richter, 1909 edition, i., 301); over manganese dioxide, or over lead dioxide; but the product in every case gave a test for phosphoric acid when hydrolysed with water, evaporated with nitric acid, and treated with the solution of ammonium molybdate in nitric acid. Phosphorus-free acetyl chloride was finally prepared by passing a rapid stream of hydrogen chloride either through a mixture of glacial acetic acid and phosphorus pentoxide (Richter, i., 300), or, preferably through purified acetic anhydride kept at  $100^\circ$  (Beilstein's "Handbuch," i., 462). Distillation over anhydrous sodium acetate easily removes contaminating phosphorus compounds from the acetic anhydride.

Satisfactory results were obtained by the use of the pure acetyl chloride when as much as 1.3 grm. of the  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was present in a mixture of 2 grms. of the hydrous chlorides. No determinations of the iron in the filtrate were made when the pure acetyl chloride was used (see Table IV.).

The precipitation of hydrous aluminium chloride by the use of the acetone-acetyl chloride [4 : 1] mixture is very simple, quick, and accurate, and affords an easy method for the exact determination of aluminium associated with iron.

In conclusion, it remains to thank Prof. Gooch for his kind advice and suggestions throughout the course of the work.—*American Journal of Science*, xxxix., p. 197.

## THE ELECTRO-TITRAMETRIC METHOD AND ITS APPLICATION TO GENERAL ANALYTICAL CHEMISTRY.\*

By F. H. HESSELINK VAN SUCHTELEN and ARAO ITANO.

SINCE the time of the first use of the empirical normal solutions of Gay-Lussac and the introduction of present normal solution of Ure, volumetric analysis has never received such a strong impulse as that through the application of physical chemistry. This is especially true for the volumetric determinations of acids and bases, in so far as the nature of neutralisation is now clearly understood. Our knowledge of the rôle which indicators may play in neutralisation has been increased in recent years very markedly by the introduction of the dissociation theory. We do not consider that this is the place to go into a discussion of indicators, but it will suffice to say here that with the knowledge of the necessary facts, especially of dissociation constants, we may occasionally predict whether an indicator is applicable in a special case or not.

In spite of the fact that in recent times the theoretical knowledge of the colour indicators has been considerably increased, and here and there practical applications drawn

from those principles have been made, there are still, as every analytical chemist knows, many embarrassing and unmanageable difficulties to contend with.

We can only touch upon a few of those difficulties. For instance, the personal equation which can cause an error of 1 cc. in a 0.01N solution, and further the difficulty encountered with a liquid which possesses a colour that may interfere with the recognition of the indicator, and those complications which may arise in the case of very dilute solutions. These are only a few of the reasons why the application of indicators in the general analytical field of chemistry is rather limited. It is therefore not unexpected that attempts have been made to overcome these difficulties by the introduction of another type of indicators which are dependent on and indicative of the physico chemical changes in the solution.

W. Böttger some years ago, in the case of coloured or turbid solutions in which the change of colour of an indicator would be more or less masked, recommended the use of the electrometer (*Zeit. Phys. Chem.*, 1897, xxiv., 253). It must be said, however, that determinations with this instrument are more laborious, and that such measurements are less familiar to chemists than the determination of conductivity. It is the merit of Küster and his associates (F. W. Kuster, M. Grütters, and W. Geibel, *Zeit. Anorg. Chem.*, 1904, xlii., 225) to have shown that such titrations, which cause great difficulty and uncertainty, could be made with a high degree of accuracy if, instead of depending on the change of colour, use was made of the change of physical-chemical property (electrical conductivity) of the liquid by the process of neutralisation. We may conclude from their work that the point of neutrality between strong acids and bases can be determined much more exactly by conductivity methods than by the use of indicators. Also, if weak acids were used, as, for example, tartaric and acetic acids, which, as is well known, have caused so many difficulties by the ordinary titration method, sharp and good results were obtained by the use of the conductivity method. The point of neutralisation of red wine by means of the conductivity determination was much more definite than if determined by titration with litmus. The attempt was also made by them to titrate four quinine derivatives by the electro-conductivity method with good success. Further, Duboux and Dutoit have used this conductivity titration in many of their special researches in wine analysis (*Journ. Suisse de Chim. et Pharm.*, 1908, p. 690). From their interesting work, which treats especially the organic acids in wine, we may say that the conductivity titration has proved here also to be a very successful and helpful aid in chemical analysis.

The preparation of exact ammonium citrate solution, which previously gave rise to difficulties, has been solved by the application of the above mentioned method by Hall and Bell, who showed by this method an exactly neutral solution of ammonium citrate was easily prepared (*Journ. Ind. Eng. Chem.*, 1911, iii., 559).

In our analysis of soil solutions, we had already used the method of titration by conductivity in determining the acid and basic binding capacity of such solutions (*52nd Ann. Rept. Mich. Board of Agr.*, 1913, p. 149). We feel that it would be superfluous here to go into the fundamental principles underlying this method of analysis, since they may be considered to be the common property of the analytical and biological chemists, and there is no lack of excellent manuals dealing with the practical phases of measurements of electrical conductivity. We will therefore confine ourselves to a brief summary of results, and call attention to precautions necessary in carrying out our technique.

It must be said that in the execution of such conductivity titrations, certain precautions have to be followed. These will be treated very briefly because such rules can be deduced easily from the theoretical basis of the applied method and from hydrolysis.

It is quite evident that in most of our experiments a determination of the cell constants did not need to be con-

\* From the *Journal of the American Chemical Society*, xxxvi., No. 9.



To those familiar with this field of work, this short introduction does not claim to disclose any new point of view, nor, for those not so well versed in these subjects in question, do we attempt an exhaustive presentation of the fundamental supporting theory.

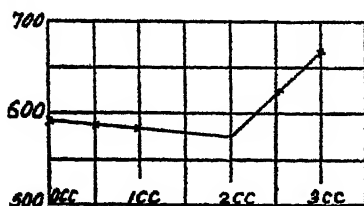


FIG. 5.—Determination of Cl.

In cup 10 cc. 0.1/N KCl.  
Titrated with 0.5'N AgNO<sub>3</sub>.

	Readings
0 cc. . . . .	592
0.5 cc. . . . .	586.5
0.955 cc. . . . .	582.3
2.000 cc. . . . .	576
2.55 cc. . . . .	629.5
3.00 cc. . . . .	668.3

Theoretically, 2 cc. = 35.46 mgrms. Cl. Found,  
2 cc. = 35.46 mgrms. Cl.

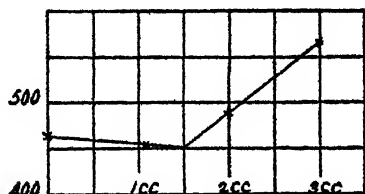


FIG. 6.—Determination of SO<sub>4</sub>.

In cup 5 cc. 0.1/N K<sub>2</sub>SO<sub>4</sub>.  
Titrated with N/3 Ba(NO<sub>3</sub>)<sub>2</sub>.

	Readings
0 cc. . . . .	463.0
1.06 cc. . . . .	452.1
2.005 cc. . . . .	485.0
2.986 cc. . . . .	567.8

Theoretically, 1.52 cc. = N/3 Ba(NO<sub>3</sub>)<sub>2</sub> = 240.175 mgrms. SO<sub>4</sub>. Found, 1.58 cc. = 240.175 mgrms. SO<sub>4</sub>.

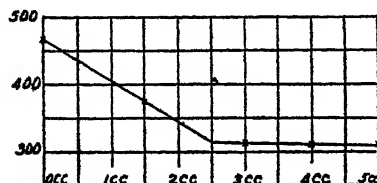


FIG. 7.—Determination of PO<sub>4</sub>.

In cup 10 cc. 0.1'N (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>.  
Titrated with 0.25'N UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>.

	Readings
0 cc. . . . .	466.5
1.5 cc. . . . .	375
3.0 cc. . . . .	311
4.0 cc. . . . .	310
5.0 cc. . . . .	310

Theoretically, 2.5 cc. contains 31.68 mgrms. PO<sub>4</sub>.  
Found, 2.5 cc. contains 31.68 mgrms. PO<sub>4</sub>.

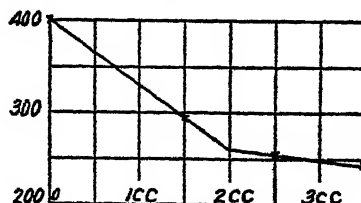


FIG. 8.—Determination of NO<sub>3</sub>.

In cup 5 cc. 0.1'N NaNO<sub>3</sub>.  
Titrated with 0.25'N C<sub>20</sub>H<sub>16</sub>N<sub>4</sub> (addition of  
1 drop 1:1 H<sub>2</sub>SO<sub>4</sub>).

	Readings
0 cc. . . . .	401
1.5 cc. . . . .	297.5
2.5 cc. . . . .	257.5
3.5 cc. . . . .	245.0

Theoretically, 2 cc. = 31.005 mgrms. NO. Found,  
2 cc. = 31.005 mgrms. NO<sub>3</sub>.

We will now proceed to consider the individual curves, and there, as the case may arise, enlarge upon certain features necessary to an understanding of the subject. We deem it advisable to start with the most simple case in our analysis, namely, the titration of acids and bases, because they may be considered as the basis of our work.

In the preceding paragraphs we have discussed some of the typical features and peculiarities of this special conductivity titration. Let us turn now to a comparison of the accuracy of this method with that of a colour indicator. We see at once that the values for neutrality, as obtained by means of phenolphthalein, are all without exception more alkaline than those determined from the conductivity titrations.

The question now arises, "Which method gives the neutral point with greater accuracy?" In deciding this question, use was made of the indicator table so thoroughly worked out by Sorensen. It was easily demonstrated that by the use of an appropriate indicator with a sharp colour change at the neutral point, results were obtained which agreed with the conductivity titration. Besides this, it is a well-known fact that the neutral point of phenolphthalein is decidedly alkaline.

It must be noted here that of the above curves, only one (No. 1) was made by an experimenter who was familiar with conductivity titrations. The others were all worked out by men performing the experiment for the first time. This fact leads to an important feature of the conductivity titration, namely, that the influence of the subjective factor which necessarily enters into every chemical analysis is here minimal. This fact will be borne out by a consideration of the above curve.

It should be added that many of these curves were made without the use of a galvanometer. It is evident that the use of this instrument will still further minimise the influence of the personal equation. The significance of this elimination is emphasised, on the contrary, by a glance at the varying results obtained by different experimenters using phenolphthalein—an indicator noted for the sharpness of its colour change.

As may be seen from the graphs, it is an *a priori* fact in conductivity titrations that they are not characterised, as are the colour indicator titrations, by a total dependence on one single point at which the colour changes. The conductivity titration, on the contrary, is typified by lines, each line being fixed and determined by a series of points, the number of which is under the control of the experimenter. We consider this to be an important advantage over the colour indicator method, for many interesting deductions can be drawn from such curves.

In regard to the point of inflection, we may say that it is sharply defined and determinable with exceeding precision. As an illustration of this, the graph (Fig. 2) may

serve. In this case 0.001 N 5 cc.  $\text{H}_2\text{SO}_4$  were titrated with 0.01 N NaOH. Even in this concentration the result was satisfactory.

In the experiment (Fig. 3) the electro-titrametric method was employed for the titration of a weak acid (lactic acid) with a strong base (NaOH)—a titration which had hitherto been attended with many difficulties.

The amount of lactic acid was determined by the formation of its zinc salt, and, in accordance with this, a normal solution was prepared (theoretical inflection point, 1 cc.; found, 1 cc.). Here again, as in the experiments described in the foregoing, the electro-titrametric method proved to be of especial value, because of the high degree of precision with which the neutralisation point was obtained. It is to be noted here that the titration in this case was performed in the reverse of the usual manner; i.e., the NaOH was placed in the conductivity cup and the acid was added to it from the burette. The reason for this procedure is at once evident and requires no comment.

The graph (Fig. 4) is an illustration of the determination of various organic acids (malic, tartaric, and succinic). It is interesting to note that in the case where no acetic acid was added (No. 1), the result was in perfect accordance with the total amount of acids present. In the determination, however, when an addition of acetic acid had taken place (No. 2), only tartaric acid and maleic acid showed their presence.

Up to now we have considered simply the determination of neutralisation points. This naturally is the most ordinary kind of determination to make first, but in no way marks the limitation of the sphere of usefulness of the method. We feel confident that the electro-titrametric method will find a constantly widening field of application, and this will naturally be a source of personal gratification to us, should it prove to be the case. The experiments which we have performed are necessarily limited in number and kind, being confined to the determination of those elements and radicals known to be of particular importance in general and biological chemical analysis.

At this juncture we wish to emphasise two points that strongly commend this method, namely, accuracy and ease of performance. The elements and radicals included in our determinations were Cl, Ag,  $\text{SO}_4$ , Ba, U,  $\text{PO}_4$ ,  $\text{NO}_3$ , K, Ca,  $\text{Fe}^{++}$ .

In the first determinations of those elements and radicals, we aimed to test the method as to its application and limitations, and we used therefore chemicals of highest purity (Kahlbaum), even going so far as to check their purity by standard methods of analysis.

The first of these experiments was a determination of Cl in KCl by means of  $\text{AgNO}_3$ . Fig. 5 shows the sharpness and precision which characterises the determination. The value obtained by the conductivity titrations coincided exactly with the theoretical value (theoretical, 35.46 mgrms. Cl; found, 35.46 mgrms. Cl).

The next analysis was the determination of  $\text{SO}_4$  in  $\text{K}_2\text{SO}_4$ . In the cup was 10 cc. N/10  $\text{K}_2\text{SO}_4$ . This was titrated with N/3  $\text{Ba}(\text{NO}_3)_2$  (Fig. 6).

At this point attention should be called to the fact that, in order to obtain the highest degree of precision, we introduced, in many instances into the cup, a very small portion of the salts yielding the precipitation to be expected. It will be seen that in addition to what has been said already, the analysis of  $\text{K}_2\text{SO}_4$  by the electro-titrametric method does away with the laborious processes of precipitation, incineration, and weighing, and avoids the many opportunities for error engendered by these operations.

The next determination was that of  $\text{PO}_4$  in  $(\text{NH}_4)_2\text{HPO}_4$ , the titration being formed with uranium nitrate as reagent. A glance at Fig. 7 shows that the analytical result agrees exactly with the amount introduced. This analysis in particular is noteworthy because of the fact that in using the ordinary indicators (cochineal or potassium ferrocyanide) the turning points are not very definite, and, in general, leave much to be desired.

Another electro-titrametric determination was that of  $\text{NO}_3$  in a solution of  $\text{NaNO}_2$  (a salt which may be looked upon as chemically pure Chili saltpetre), containing also free  $\text{H}_2\text{SO}_4$  (Fig. 8). This solution was titrated with a 0.25 N solution of nitron in acetic acid. In this experiment, where the theoretical amount of nitrate present was 31.005 mgrms., the electro-titrametric method again showed perfect coincidence. A differential determination of nitrates and nitrites is possible by the use of hydrazine sulphate.

(To be continued).

## PURE BREAD AND FLOUR.

MEMORIAL to the Right Hon. HERBERT LOUIS SAMUEL, P.C., M.P., President of the Local Government Board.

As bread and flour form about two-fifths of the weight of food consumed by the working classes, and constitute the principal diet of many poor children, it is of the utmost importance that the people should be able to obtain bread made from genuine whole meal or wheat meal (a grade from which a little of the coarse bran has been removed) ground to a uniform fineness, so that the digestive juices can surround the particles and extract their nutriment.

When these meals cannot be assimilated, it is advisable to encourage the use of household flours containing the maximum nutriment of the wheat grain that can be obtained with a smaller amount of indigestible woody fibre.

The Council of the Bread and Food Reform League and a number of ladies and gentlemen consider that the distress caused by the war and the increased cost of food make this subject of such urgent and national importance that they venture to bring under the notice of the President of the Local Government Board the desirability of encouraging the consumption of these breads.

Recent scientific investigations prove that serious disease is produced by minute alterations in food stuffs, and that the vitamins found in whole meal, wheat meal, and old-fashioned household flour (but removed from fine white flour), are most important elements of nutrition when bread forms the principal food.

As practical experience shows the beneficial results secured by the use of these breads when genuine, the memorialists wish to also urge the importance of measures being taken to prevent the abstraction, without notification to the public, from whole meal, wheat meal, and household flours of the "germ" of wheat, and the strong gluten found in flours commercially designated "patents," used for the production of expensive breads.

SUGGESTIONS made by the COUNCIL OF THE BREAD AND FOOD REFORM LEAGUE in connection with the foregoing MEMORIAL.

(1). The Council desire to direct attention to the great importance of measures being taken to prevent flour being artificially bleached with chemicals. If this cannot at present be accomplished, the Council wish to inquire if it would be possible, by an Order of His Majesty in Council, or in virtue of the powers now given to the Government, to make it obligatory that all flours artificially bleached with chemicals or containing so-called "improvers," baking powders, or other chemical ingredients, shall have a notification of this fact on the sacks in which they are sold, and that bakers using such flours shall state prominently in their shops that their bread is made from bleached flour or contains chemical ingredients, in the same way as a notice about the use of sterilised cream is shown in dairies.

Enormous quantities of flour are now bleached artificially by a chemical process which is condemned by most eminent scientists and by a large number of millers. "Bleached flour cannot be supplied under any conditions



to American citizens, but can be sent abroad to those foreign countries whose laws allow it to be dumped upon them. Of these our own country is one" (Benjamin Moore, M.A., B.Sc., F.R.S.). Bleaching confers no advantage in nutritive properties or flavour upon the flour. It simply enhances the profits of the millers. It is of no value, and the large sum spent upon bleaching flour is a national waste.

The Bread Act in Section II. provides that bakers shall make bread of flour or meal with "any common salt, pure water, eggs, milk, barm, leaven, potatoes, or yeast, and mixed in such proportions as they shall think fit, and with no other ingredient or matter whatsoever, subject to the regulations hereinafter contained."

Section VIII. provides that no baker "shall at any time or times in the making of bread for sale use any mixture or ingredient whatsoever in the making of such bread other than and except as hereinbefore mentioned on any account or under any colour or pretence whatsoever."

Millers or bakers who add anything but the above-mentioned ingredients to meal or flour or bread can by this Act, which has not been repealed, be punished by a fine.

(2). The Council wish also to suggest that the Local Government Board might advise relief committees, children's care committees, institutions, &c., to use a bread made from finely ground genuine whole meal, wheat meal (from which some of the coarser bran has been removed), or a household flour containing at least 80 per cent of the grain, including the "germ" and all the "patents."

The Council would also suggest the advisability of these breads being used for Belgian refugees or Germans who are interned or are prisoners. They would probably prefer these breads to white bread, as brown bread is used by Belgians and Germans.

The Council wish to direct the attention of the Local Government Board to the following facts:—

That for nearly forty years bread has been used in prisons made from meal "consisting of all the products of grinding the wheaten grain with the exception of 12 per cent of coarse bran and coarse "pollard." ("Prison Rules" made by the Secretary of State under the Prisons Act).

That over two and a half million meals containing whole meal bread have been supplied to the poorest children in London. That the Rev. Canon Horsley (who has supervised the distribution of over a million and a quarter of these meals) and a head master (one of the first to start these dinners at a poor London school, where 150,000 meals have been provided) say that they have had no complaints of physiological disadvantages arising from the use of finely ground whole meal bread, and that the continuous reappearance year after year of the same children proved its popularity.

That the 80 per cent old-fashioned household flour has been used at Christ's Hospital (Blue Coat School) since the meeting of the Bread and Food Reform League at the Mansion House in 1907, and that the authorities are so satisfied with the result that they use it exclusively, even for cakes and puddings.

(3). The Council desire to direct attention to the importance of paragraph 9 of the Food and Drugs Act, 1875, being enforced with regard to meal, flour, and bread, especially whole meal, wheat meal, and old-fashioned 80 per cent household flour, now generally known as "Standard," and the breads made therefrom. This section of the Act provides:—

That no person shall, with the intent that the same may be sold in its altered state, without notice abstract from an article of food any part of it so as to affect injuriously its quality, substance, or nature."

There is a recognised quality for the above meals and flours in Governmental publications, and Mr. C. F. Lloyd, barrister, states in the 1914 edition of Bell's "Sale of Food and Drugs Act":—

If the article demanded has some recognised standard of quality or composition it is an offence against the section (VI.) to sell an article which does not come up to that standard.

The Local Government Board Report on the "Nutritive Value of Bread made from different Varieties of Wheat Flour" mentions that 80 per cent "Standard" flour should be a "straight run" flour, from which coarse branny particles amounting to about 20 per cent of the whole grain have been removed, and containing the whole of the contents of the endosperm, the germ, and a certain amount of finely comminuted branny particles and cell walls of the endosperm.

The Report mentions that much of the 80 per cent "Standard" flour sold is a mixture of low-grade flour, from which the "patents" have been removed, and finely divided offal. "Such flour can be made at a cost of from 2s. 6d. to 3s. per sack less than an 80 per cent straight run; the pecuniary gain which the miller can effect in this way is considerable."

In order to illustrate the prevalence of this custom with regard to whole meal and wheat meal, it may be mentioned that the "Book of Bread" states that by some millers "anything is considered good enough for meal," and owing to the sale of mixtures of white flour and offal advises bakers that "the safest plan is to sell the bread as 'brown' and not 'whole meal,' and this is very much more frequently necessary than many consider."

The Local Government Board Report states:—"The ordinary tests as to appearance and colour as applied by millers may serve, in the hands of those accustomed to examining milling products, to detect the difference between a genuine 'Standard' and an 'imitation Standard' flour from the same wheat." "It is obvious that there may be particular instances in which neither the trade expert nor the analyst need have any difficulty in pronouncing that a flour is so different from any flour of the 'Standard' class that it cannot properly be termed 'Standard' flour, and similarly with 'Standard' bread. Chemical analysis in regard to fibre, mineral matter, &c., may, of course, be of great value in cases where it is desired to know if the flour supplied complies with a given specification or corresponds to sample, and the utility of analysis for this purpose is likely to increase with the attention which is now being given to the matter by chemists." Further physiological and chemical tests or other methods could probably be evolved which would show even more clearly whether the "germ" and "patents" are retained in meal and flour. The above remarks will also probably apply equally well to whole meal and wheat meal bread.

The German Government has recently ordained that wheat flour must contain 75 per cent of the total weight of the grain, and the manufacture of bread containing 80 or 90 per cent is suggested in a pamphlet on the "Food Supply of the German People," published by Dr. Eltzbacher, of Berlin, and fifteen other collaborators (reviewed in the *Lancet*, February 20, 1915). It is there stated, with regard to the use of bran for animals, which can be fed on other substances:—"The separated bran, if employed for human consumption through an animal, loses at least 50 per cent of its total value."

"*Patents*."—Millers usually obtain in the present roller mills about 70 per cent of what is technically called "a straight run flour," but which does not include the "germ," as it should do. This amount may vary in different wheats from 55 to 75 per cent. After extracting the "straight run flour" a residue is left which is now generally used for feeding cattle, and contains a large amount of phosphates and important "vitamines."

This 70 per cent straight-run flour is usually sub-divided into what are technically called "patents" and "households" or "bakers" flours. The amount extracted for "patents" varies from 18 to 42 per cent, dependent upon the wheat used and the methods of milling employed.

The residue sold as "bakers" flour contains a trifle more protein than the "patents," but the gluten in the "patents," although a little smaller in quantity, is of a "stronger" quality. Gluten, which is stated by eminent chemists to be composed of gliadine and gluten in varying proportions, is the special constituent of wheat which makes it preeminently suitable for making bread. Bakers find the gluten in "patents" more tenacious and tougher than that found in "bakers" flour, and state that it makes a better aerated loaf. "Patents" are used for fine, expensive white breads, and also for mixing with lower grade flours.

Chemical analysis does not always indicate the dietetic value of a food. Although the "patents" contain slightly less protein than "bakers" flour, there is reason to believe that the gluten in the "patents" is of a superior quality. Alderman Jago, F.I.C., states in "Modern Developments of Bread Making" that although chemical analysis indicated that "bakers" flour, from which the "patents" had been abstracted, had a little more protein, artificial digestion showed there was a larger amount of digested proteins from "patents" and "straight run" flour which includes the "patents," than from "bakers" flour from which they are extracted. As it is generally agreed that the body requires different kinds of proteins, whole meal, wheat meal, and household breads should not be deprived without notification of the highly developed gluten found in the "patents," which also improve the palatability, digestibility, and appearance of the bread and also probably make it more satisfying. As the amount of protein in different wheats varies from 6.9 per cent up to 24.2 per cent, it is very important that thoroughly cleaned wheat of good nutritive quality should be used, and millers have learnt by long years of thought, study, and experiment to mix wheats and blend flours so as to combine the varying qualities of different wheats.

There is only about 24 per cent of indigestible fibre in the wheat grain, and when meal is ground to a uniform fineness the digestive juices can surround the particles of bran and extract their nutriment. Moreover the presence of this small amount of fibre in bread is, when finely ground, most beneficial for some persons, in preventing the serious evil of constipation. The late Sir Henry Thomson stated in "Food and Feeding," "The extraordinary care which is taken to employ nothing in our diet but matter which has nutritive value—that is, can be absorbed into the system—is founded upon want of knowledge of the first principles of digestion."

The Bread and Food Reform League advise those who cannot digest whole meal even when finely ground to use the old-fashioned 80 per cent household bread, now generally known as "Standard." Dr. Robert Hutchinson states in "Food and Dietetics," (1911), with reference to this bread that it "is certainly superior to ordinary white bread from a chemical point of view, whilst it is in no way inferior to the latter in digestibility and capability of absorption."

**Vitamines.**—It was pointed out at the International Medical Congress that recent discoveries have revolutionised the former conception of nutrition in man and animals. Albumens, carbohydrates, fats, salts, and water were not alone sufficient, but certain other substances normally present in most minute quantities were also essential. Dr. Hopkins, F.R.S., mentions that minute quantities of these substances "allow our systems to make full use of the building elements of the grain," whilst the *Lancet* in an article on the "Physiology of the Minute quantity," refers to "the remarkable action of small entities in the human body."

Drs. Edie and Simpson, of the Liverpool School of Tropical Medicine, state:—"It has been proved by Baddon and other workers in the East that exclusive use of polished rice as a diet leads to the production of that form of peripheral neuritis which we call beri-beri, and that this disease does not occur in those native races who use the whole rice as a diet." Their experiments show

that "parallel results are obtained when the outer layers are excluded from the diet with both wheat and rice. These experiments clearly demonstrate that the outer part of the grain contains an essential constituent for the nutrition of the nervous system both in growing animals and adults."

Prof. Leonard Hill, F.R.S., who has directed much attention to these vitamins, states in the *British Medical Journal*:—"To grind the wheat, and take away not only the germ—the very embodiment of growth—but to impoverish the flour in most of the essential organic phosphorous compounds contained in the outer layers, seems a most extraordinary manipulation of the Staff of Life."

"More extraordinary still is the fact that the State allows this to be done, and does not insist on the miller notifying that the flour has been thus impoverished. If such a thing were done to any other article of food the law surely would step in."

Owing to the inferior quality of much whole meal, wheat meal, or 80 per cent old-fashioned household flour, the Bread and Food Reform League never mention the name of any baker unless they have a guarantee from the millers supplying him as well as one from the baker. Bread is now an anonymous mixture, and it might possibly safeguard the public, as well as conscientious millers and bakers, if bakers were obliged to state in their shops the names of millers supplying them with meal and flour.

(4). The Council desire to urge the importance of Foods Inspectors being instructed to direct their attention to supplies of whole meal, wheat meal, and old-fashioned household bread (now generally known as "Standard") and bread made therefrom being of genuine quality, that they retain the germ, have had none of the "patents" extracted, and that they have not been bleached or contain so-called "improvers," baking powders, or other chemical ingredients without notification to the public.

The Council wish to direct the attention of the Local Government Board to the fact that whereas only 70 tons of white flour are usually made from 100 tons of wheat, 88 tons of the better and more nutritious flour can be obtained. This is an increase of more than 25 per cent, an important fact in war time.

## REPORT OF THE BRITISH SCIENCE GUILD WITH REFERENCE TO THE MANUFACTURE OF OPTICAL INSTRUMENTS AND MATTERS RELATING THERETO.

### NECESSITY FOR ACTION.

THE British Science Guild, having enquired carefully, by means of a strong and representative expert Committee, into the effect of the outbreak of hostilities on matters of national importance connected with the manufacture of optical instruments in the country generally, submits this report to the Government, and in doing so emphasises the pressing urgency of the subjects referred to.

### Supply of Glass. (a). The General Case.

1. In the first place the enquiry referred to was directed to the consequences of the sudden stoppage of the supply of German optical glass on which this country had increasingly relied for many recent years. A letter of enquiry asking for information on six specific points was addressed to representative firms in the optical trade. The results of these enquiries has been such as to satisfy the Guild that the supply of optical glass available for the manufacture of telescopes, binoculars, range-finders, and other service instruments is sufficient for the purpose. Under this head there seems to be no call for any special effort to improve upon existing conditions, though the supply of English glass has not always been adequate in

quantity, and delays have been experienced in obtaining quick delivery.

The representative of Messrs. Chance Bros., who was a member of the Technical Committee referred to above, has assured the Committee that since the outbreak of hostilities the firm has considerably increased (in fact, quadrupled) the capacity of its plant for the manufacture of optical glass, and is fully prepared to extend this plant still further.

(b). *Photography and Micrography.*

2. With regard to the manufacture of photographic and microscopic lenses the case stands otherwise. The requirements of the manufacturing trade in these respects are not definitely standardised as in the case of the instruments already referred to. To facilitate new and important developments it is necessary that the lens manufacturer should have recourse to a greater variety of glasses than are in fact manufactured at the present time in this country. It is further necessary that larger stocks should be held than is the custom at the present time of the various glasses produced. The Guild, therefore, is of opinion that serious inconvenience is certain to result to the manufacturing trade if the supply of German glass is cut off for any considerable length of time. The amount of glass demanded, especially for photographic purposes, is very considerable, and the Guild is of opinion that the attention of the authorities might usefully be drawn to this opportunity for a considerable development of British glass manufacture in this direction. One difficulty the Guild understands to be the defective supply of pure barium compounds.

(c). *Variety of Glass Obtainable Inadequate.*

3. From a wider point of view and more generally, the variety of English glasses offered is not sufficient for all the requirements of optical instrument makers, especially for the more recently developed and important optical designs. Thus, whilst the English leading firm listed only 20 to 30 types of glass, the leading German firm listed about 70 types, every one stocked. Barium glass of high refraction and low dispersion, i.e., having a high value of the "anti-dispersion" coefficient, is reported as specially difficult to obtain in England.

*Research.*

4. The desirability of the provision of facilities for research upon the manufacture of optical glass has been carefully considered and has been found to be a difficult question. From the evidence submitted it appears that if one special object of research could be attained the result would be highly advantageous. This object is the discovery of a refractory lining of the melting "pot" which would resist the action, at melting temperatures, of the materials used in the glass mixtures, and leave the contents of the pot uncontaminated at the conclusion of the operation. This research would probably be a long and costly one, and is such as might most appropriately be undertaken by the National Physical Laboratory, especially as certain details in the manufacture of optical glass may come under review during the enquiry.

*Authoritative Testing of Glass.*

5. In another direction evidence was submitted to the Guild to the effect that it would be distinctly advantageous to the optical trade if increased facilities for the authoritative determination of the optical constants and relative absorption of samples of glass submitted for test could be provided at the National Physical Laboratory.

*THE FUTURE.*

*Facilities for Education a Matter of Great Urgency.*

6. In still another direction evidence, additional to evidence collected before the outbreak of hostilities, was elicited that the facilities for education in technical optics

are very inadequate. It was shown that not only could some of the present difficulties connected with the supply of optical glass probably be diminished, but that the output of optical instruments for national purposes would be increased, and that the optical trade would be substantially benefited in other directions if such facilities were largely extended. The Technical Optics Committee of the Guild was originally appointed, early in the year 1914, for the purpose of "enquiring into the need of an Institute of Technical Optics and the steps to be taken in connection therewith" and in due course it submitted a "statement" on the subject, which was published in the Annual Report of the Guild, 1914, pp. 31-34. The Committee had further reported to the Executive Committee of the Guild at its July meeting, and the report was adopted with a few alterations, and is printed at the end of this report.

7. When the Technical Optics Committee met after the vacation, the other matters, apparently of more immediate urgency, referred to in this report had arisen and took precedence of the earlier matter. In investigating these new questions it has become strongly evident that the earlier matter is of supreme and pressing importance.

The Guild therefore recommends:—

- A. That better provision should be made at the National Physical Laboratory for the testing of samples of glass as to their physical and optical properties, and that the Director of the National Physical Laboratory be approached on the subject.
- B. That facilities should be provided as speedily as possible for the carrying out, at the National Physical Laboratory, or elsewhere, of the researches connected with the manufacture of optical glass referred to in this report.
- C. That steps should be taken as speedily as possible to give effect to the recommendations of the previous report of the Technical Optics Committee of the Guild in the direction of providing facilities for systematic, scientific, and manual training in Technical Optics, and the Guild, recognising that educational training requires time, is strongly of opinion that this question is urgent and that the organisation of optical training should be taken in hand at once.

*PREVIOUS REPORT REFERRED TO IN PARAGRAPH C,  
DATED JULY 14, 1914.*

*Proposed Establishment of an Institute for Technical Optics.*

The British Science Guild has had under consideration for some time the inadequate provision for, and the unsatisfactory state of, the technical training in optics in the British Isles. The subject was brought to its notice by Sir Thomas Barlow, K.C.V.O., formerly President of the Royal College of Physicians, in a communication to the President of the Guild, and was considered to be of such importance by the Executive Committee that a Special Committee was formed to deal with it. The Special Committee has now reported.

The establishment of such an Institute has been under discussion for some years, and there is a remarkable consensus of expert opinion, both as to the necessity and the urgency for action, from many and diverse points of view, scientific, industrial, and national.

The London County Council, which has gone into the matter very thoroughly, has not felt itself in a position to provide from the funds under its control the initial capital expenditure of some £40,000 for the erection and equipment of the proposed Institute, although a site was actually purchased for the very purpose by the Governing Body of the Northampton Polytechnic Institute as far back as 1908. The Finance Committee of the Council is understood to be of opinion that the project is so essentially of national importance that it would be unfair to saddle London ratepayers with the whole cost. It is, however, believed that if the question of capital expenditure can

be solved, the maintenance of the Institute could be assured by grants from the Board of Education and from the London County Council, and by students' fees. As an additional reason for expedition, it may be pointed out that the Governing Body of the Northampton Polytechnic Institute may not be in a position to carry much longer the heavy burden of the mortgage interest on the purchase money above referred to, and the amortisation of the capital amount.

## INDUSTRY AND SCIENCE.

WITH reference to the Conference which was held at the Mansion House on March 25th under the auspices of the Institute of Industry and Science of Great Britain and Ireland, we are officially informed that the Institute has received many inquiries as to the methods which it proposes to employ to carry into effect the application of organisation, science, and scientific methods to British industry at the conclusion of the war.

It will be remembered that Sir Philip Magnus made a similar inquiry at the Conference at the Mansion House.

A very effective method has been evolved, but it is not the intention of the directors to disclose the details at present. The campaign initiated by the Institute has been divided into three phases:—

- (1) The creation of the Institute and an organisation.
- (2) To consider and disclose the weak points in the working conditions in which British industry at present operates. To suggest a new basis, and have it generally approved by leading men of industry, science, and finance.
- (3) To draw the attention of all concerned to the problem, and to create a general inquiry as to the method to be adopted to give effect to the new basis.

Apart from the good sense shown in proceeding by stages, the general object in view is to make people think and inquire. Items (1) and (2) have already been successfully accomplished, the first at the Savoy Hotel last October, and the second at the Mansion House on March 25th.

The details of the new basis are put forward in the book on "First Principles of Production," by J. Taylor Peddie, F.S.S., and others, just published by Messrs. Longmans, Green, and Co., and all who are interested in the question are asked to read the book.

Inquiries are now being made with regard to the third and last phase, but this will not be disclosed until the dinner, which is to be given in about a month's time to leading industrialists, scientists, and bankers.

In view of the important position held by the gentlemen constituting the Court of Directors in the various industries of the country, it may be taken for granted that it follows essentially practical lines, and will be effective.

Industrial and scientific organisations will greatly appreciate the details of the new scheme as soon as they are disclosed.

## CORRESPONDENCE.

### CHEMICAL APPOINTMENTS.

To the Editor of the Chemical News.

SIR,—I should like to know if the appointments of analytical chemists are at all likely to be given to women. Would an application from a science graduate, with chemistry as a final subject for the degree, be considered.—I am, &c.,

EVELYN K. WILLIAMS.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, March 4, 1915.

Prof. W. H. PERKIN, LL.D., F.R.S., President,  
in the Chair.

MESSRS. R. G. Fargher, A. J. Boyd, H. Shulman. S. H. Ting, and J. G. F. Druce were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Henry Jackson Evans, B.Sc., Brockenhurst, Christchurch Park, Sutton, Surrey; Nikolai Semenovitch Kurnakov, Institute of Mining, Petrograd, Russia; Thomas Dagomet Morson, 16, Elsworth Road, Primrose Hill, N.W.

The names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council, 1915-1916, were read from the Chair.

The following papers were read:—

"*Syntheses of Benzo  $\gamma$ -pyrones and Flavones.*" (Part I.). By SERGE JACOBSON and BROJENDRANATH GHOSH.

"*Formation of Coumarin Derivatives and the Production of Stable Coumarinic Acids.*" By LOUIS ARNOLD JORDAN and JOCELYN FIELD THORPE.

Ordinary Meeting, March 18, 1915.

THE PRESIDENT referred to the loss sustained by the Society, through death, of George Price Dodda, Henry Durham, Edward Gillman, Frederick Ernest Pollard. William James Sell.

Messrs. Frederick A. Mason and Ronald MacInnes were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. John Lloyd Bentley, 48, East Mount Terrace, Darlington; Premananda Das, 76 and 77, Sukea Street, Calcutta, India; Robert Edward Forbester, M.Sc., 91, Wingrove Avenue, Newcastle on Tyne; David Charles Roberts, 43, Rufford Road, Elm Park, Liverpool.

The following papers were read:—

"*The Relation between Viscosity and Chemical Constitution.* Part IX. *The Viscosity and Fluidity of the Aliphatic Acids.*" By ALBERT ERNEST DUNSTAN.

"*Velocity of Crystallisation from Aqueous Solutions.*" By NORMAN PHILLIPS CAMPBELL.

## MEETINGS FOR THE WEEK.

TUESDAY, 13th.—Royal Institution, 3 "The War on Architecture," by Banister Fletcher, F.R.I.B.A.

THURSDAY, 15th.—Royal Institution, 3. "The System of the Stars," by Prof. A. S. Eddington, F.R.S.

FRIDAY, 16th.—Royal Institution, 9. "The Russian Idea," by Stephen Graham.

SATURDAY, 17th.—Royal Institution, 3 "Modern Artillery," by Lieut.-Col. A. G. Hadcock, late R.A.

## ALFRED JÖRGENSEN LABORATORY FOR THE PHYSIOLOGY AND TECHNOLOGY OF FERMENTATION.

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# THE CHEMICAL NEWS.

Vol. CXI., No. 2890.

## THE CYCLIC EVOLUTION OF THE CHEMICAL ELEMENTS.

### PART II.

By F. H. LORING.

We have seen that certain of the elements may have been evolved by a cyclic process, which, in its graphic representation, has been likened to a complex hysteresis loop, as shown by Prof. Ewing in his book on magnetic induction in iron, &c. (See Part I., CHEMICAL NEWS, cxi., 157).

Referring to Fig. 3, we have now to consider the representation of the elements missed out in the completed diagram,\* since these are supposed to have been evolved separately, and to belong to another similar, but probably narrower, complex loop.† Such a loop might in places describe the same paths as the one illustrated, and consequently involve the additional evolution of elements similar to those already shown.

It becomes difficult to trace out the tortuous course of this series of loops, but an attempt without resorting to a diagram may have some suggestive interest.

The first element of this new series may be lithium; that is to say, one of its component sets of associates, owing to the first loop possibly taking an early upward course just where the lower atomic weight associates would appear—if the line of evolution had continued, as shown in Fig. 3. What the spectrum of such an element might be we cannot say, but in all probability the *very low* atomic weight associates, if separated from their companions of higher or lower relative atomic weight, or separated from those of another complex cycle, would show some spectroscopic difference, and this may account for certain nebular lines observed: those which have not been reproduced or verified in the laboratory with known elements. We must not, by the way, forget that temperature also plays a part in these phenomena.

The next element would be helium, assuming that this narrow cycle has some subordinate loops which extend to the zero valency line.

Continuing this complex cycle, in which we will represent the higher atomic weight associates in heavy-face type and the corresponding lower ones in light-face type, we have—

Mg—Na—Ne—Ne—Na—Mg:Ca—K—Ar—Ar—K—Ca  
:Fe—Ni—Fe—Ni—Co: Pd—Pd—Rh—Rh—La—Ba—  
—Cs—Xe—Cs—Ba—La—Cerium,

and the elements of the rare earths, followed by a side-loop taking iridium and platinum. Coming now round on the reverse side of the cycle (below the horizontal zero line, say, on the right-hand side) we have Ta—W—Os—Os—W—Ta, if these members belong to this complex loop. We have to consider the valency sequence as reversed on the lower side.

It is exceedingly difficult to discuss satisfactorily the characteristics of this series of narrow loops, but it seems to suggest that the elements of this cycle were formed

somewhat according to the theory of stellar evolution. Iron, for example, appears very early in the stars which are supposed to be of less advanced formation, and here, too, in our narrow complex loop, iron appears at an early stage, namely, as the ninth element, if the early subordinate loops extend to the zero line.

If the early loops round up, so to speak, before reaching the zero owing to some stress or strain—to borrow ideas from magnetic phenomena—then of course the number would be even fewer.

Lithium proper appears in the more advanced stars, as if the first loop of Fig. 3 had completed itself and had continued on, which would be the case in the stellar evolution where nitrogen and oxygen appear.\*

The rare-earth elements seem to partake of the short-loop characteristic peculiar to this narrow complex cycle, and these loops may be represented as a succession of small ones similar to those shown in Prof. Ewing's book on p. 346, Fig. 157. The Fe—Rh—Ir—groups are of the highly contracted type.

It is perhaps suggestive to study magnetic phenomena whilst keeping in mind the ideas here indulged in; but, of course, we must remember that a set of curves having certain hysteretic peculiarities might be obtained without recourse to electrical or magnetic circuits at all. It would seem, nevertheless, unnatural to get away from molecular or even electric influences, so that our analogy from these points of view seems reasonable. It is only a step from the atom to the molecule; indeed, some atoms *are* molecules, and the atoms themselves are electrically constituted.

The question of duality in the atomic type, or the composite nature of the elements, is one to which radio-activity leads up, and Prof. Soddy's observation that there are chemically and electrically identical atoms, though differing in atomic weight, certainly finds extended verification amongst the many radio-elements or radio-atoms, and such atoms or elements are impossible of separation by known means. On the other hand, there are identical elements in regard to atomic weight, yet having different electrical activities, and consequently chemical properties, and these are found to be quite easy of separation.

Sir William Crookes's early suggestion that our relative atomic weights may turn out to be mean numbers seems on the point of verification, to some considerable extent at least. We are, of course, familiar with his conception of meta-elements.

The discovery by Sir J. J. Thomson of a companion gas to neon having an atomic weight of 22 and existing in small relative quantities to neon of atomic weight 20 is highly suggestive, since ordinary composite neon of mean atomic weight 20.2 may be made up thus:—

$$20 \times 10 = 200$$

$$22 \times 1 = 22$$

$$\text{II) } 222$$

$$20.18$$

The mean value is close to the experimental one, and, moreover, Fig. 3 naturally accommodates these two meta-elements or associated atoms, which have been designated *neon* and *meta-neon*.

Passing to the other end of the loop we have chlorine, which may be also composite, thus:—

$$35 \times 10 = 350$$

$$40 \times 1 = 40$$

$$\text{II) } 390$$

$$35.454$$

\* The completion of the diagram shown by Fig. 3 in respect to the left-hand subordinate loops involves the inclusion of Au, Hg, Tl, Pb, and Bi in the top loop, and of Sn, Sb, (Te), and I in the middle one along with those shown.

† By the expression "complex loop or cycle" is meant a series of connected subordinate loops or offshoots.

‡ Italicised symbols are here introduced to indicate members which are possibly homogeneous in not being made up of associates or isotopes differing materially in atomic weight. This will be understood by referring to Fig. 3, where the two types are shown, though on the wider complex cycle.

\* There is a peculiarity in the early part of the other curve, as shown by Fig. 3, which would seem to point to an element of *about* atomic weight 3, but this may be a beryllium associate or satellite, unless we consider H<sub>2</sub> as a pseudo-element and assign it to this place.



This figure also agrees with experiment. In fact, it coincides exactly with the Richards-Villard classic determination of chlorine, though exact agreements are, as a rule, a little distressing when we know there must be some uncertainty in the measurements.

In the same experiment, using lithium chloride, the value for the alkaline metal came out 6.94 instead of 7.00. This was rather to be expected, since the whole-number value was regarded by some as too high. The true mean value may be as low as 6.928.

We thus see that lithium may be composite, whereas such elements as H, He, C, N, O, and F appear to be homogeneous in atomic weight and practically whole numbers, thus (taken in the same order):—1.0078, 4.00, 12.003, 14.007, 16.000, 19.0.

The fact that sodium, 23.00, is a whole number is not against the scheme, because occasionally the associates may give rise to mean values which are exactly whole-numbers, as in the possible case of arsenic, thus:—

$$\begin{array}{r} 72 \times 3 = 216 \\ 76 \times 9 = 684 \\ \hline 12) 900 \\ \hline 75.000 \end{array}$$

The experimental value in this example is 74.96, which is very close to the figured one, considering the magnitude of the number involved.

The question now might be raised, *Are we sure that H, C, N, O, and F are practically whole-number or integer elements?* The experimental evidence that such is the case is overwhelming with regard to every one of these elements except fluorine. A method of co-ordinating certain elements has been devised which involves taking the atomic weights of these elements as practically whole numbers, thus bringing all four or five members, including fluorine, into harmonious relationship. The method consists in arranging certain elements in quaternary series; for the full development of this method, see CHEMICAL NEWS, 1913, cvii., p. 95; cviii., pp. 188, 247, and 305. It is only fair to remark that this special treatment is punctuated with some uncertainties, but the above-mentioned elements are in satisfactory accord.

We will now consider the adverse side of the problem by quoting from Sir J. J. Thomson's "Atomic Theory," page 10:—"By means of the electric spectrum [positive-ray method] we can prove in a very direct and striking way some of the fundamental truths about the Atomic Theory. For example, when we form the electric spectrum of a mixture of gases, such as the air, we get a limited number of sharply-divided streams, which show no tendency to merge into each other. This shows that the gas contains only a few kinds of particles, and that all the particles of one kind have exactly the same mass, for if there had been any variation in the masses the streams would have been fuzzy. This shows that all the atoms of an element are alike; this had sometimes been questioned, and it had been suggested that there might be considerable variation in the masses of the atoms of the same element; ordinary chemical analysis could not settle this question, for it gives nothing more than the average mass of billions of atoms."

On page 16, Sir J. J. Thomson goes on to say:—"Since the atomic weights of the elements show that in their formation a measurable change of mass has taken place, the changes of energy involved in the formation of the elements must be enormous compared with those liberated in any chemical changes with which we are acquainted. Let us take an example:—The atomic weight of chlorine is 35.5; this is not a whole number; it differs from the nearest by half a unit; it follows, therefore, that in the formation of 35.5 grms. of chlorine there must have been a change of mass of at least half a grm. This involves the liberation or absorption of an amount of energy equal to that possessed by half a grm. moving

with the velocity of light, i.e.  $2.25 \times 10^{20}$  ergs. This is about the amount of work required to keep the *Mauretania* going at full speed for a week, and must have been stored up or liberated from 35.5 grms., or about one ounce of chlorine. We see that changes in the atom large enough to change the chemical character of the atom—i.e., to split an atom of one element up into different kinds of atoms—involve enormous transformations of energy; in fact, the explosion of the atom in a few pounds of material might be sufficient to shatter a continent. We are living in the midst, nay, are made up of quiescent volcanoes; fortunately their slumbers are very sound."

When we consider that, so far as published accounts of positive-ray experiments extend (see "Rays of Positive Electricity," by Sir J. J. Thomson, 1913, Longmans, Green, and Co.), they are, except in the case of chlorine, practically confined to the very elements in our diagram which have of necessity no associates differing in atomic weight (apart from the two neons, which are in satisfactory agreement), we begin to wonder whether the explanatory theory Sir J. J. Thomson has applied to this element, by way of example, affords a fully correct interpretation of facts. We must hesitate about questioning so great an authority, but there are others in great authority who seemingly take a different point of view; at least Prof. Soddy's findings in radio-activity, and Sir William Crookes's idea of meta-elements, offer a different solution, as we have already seen.

We used the word "practically" in the foregoing paragraph because, adhering to our theory, some of the associates differ so little in atomic weight that they would not in all probability give a separate and distinct positive-ray line on the photographic plate. In fact, Sir J. J. Thomson says on page 54 in his book cited:—"As  $m/e$  for this atom is 27.5, and for the nitrogen molecule 28, the lines would be so close together that it would be difficult to differentiate them." Take argon, for instance, having associates or isotopes of atomic weight 39 and 40 (ratio, say, 1:10). These would give very close lines on the plate. There is another consideration, however, in this case. The "40" line might be confused with the neon one, as, assuming that the "40" line represents a particle carrying two charges, it might then be taken for neon with one charge, presupposing that no other determining feature enters into the experiment. This observation seemingly applies also to the "40" line of chlorine. Radio-activity has revealed atoms of identical atomic weight but of different electrical composition or active constitution, therefore chemically different, so that the two 40's need not represent a real difficulty, assuming that they have a real existence. Referring to Fig. 3, it will be seen that their formation is represented to take place at widely separated times or places.

It is certainly extraordinary to consider a gaseous element like chlorine as having two sets of atoms differing by five units from each other, and co-existing in a ratio of 1 to 10, yet radio-activity gives almost such a case in the mixture of the radio-gas-atoms, and Fleck's experiments on condensation (*Phil. Mag.*, 1915, xxix., p. 337) lead us to suppose that the thorium and radium emanations, or, in our minds, their component associates (CHEMICAL NEWS, 1914, cix., p. 241), are non-separable by condensation. Fleck cites Aston's failure to separate neon from meta-neon by fractional condensation (see *Engineering*, 1913, xcvi., p. 423). Aston appears, however, to have effected a separation by diffusion through a porous substance, which would suggest that the chlorine associates might be separated by some such method if they really exist.

Be this as it may, evidently things are not quite as they seem, and electricity apparently conditions the atom in more ways than one.

The idea of extending the isotopes into the domain of ordinary elements (Soddy) is certainly supported by the argument of evolution of the chemical elements here given, and this, moreover, is founded mainly on the ideas advanced many years ago by Sir William Crookes.

ELECTROLYTIC REFINING OF GOLD.\*

By Sir THOMAS KIRKE ROSE.

In thanking you sincerely for the great honour which you have conferred on me, I have to confess that I am somewhat daunted when I reflect on the distinguished merits of each one of our past presidents. I am, however, at any rate, the equal of my predecessors in my desire to serve the Institution, and I am trying to forget any doubts I may have as to my ability to do so in this high position.

At this meeting, as in all our doings, our thoughts fly, whether we will or not, to our compatriots who are fighting our country's battles. The long list of those belonging to our Institution who are engaged in the service of the Empire shows that no stimulus is required in our profession to make its members willing to give themselves up at the call of patriotism. For the men who have fallen our hearts are filled with reverence, and our profoundest sympathy goes out to those who are stricken by their loss.

We who are left on one side, undisturbed save in mind by the clash of arms, cannot do better than continue as serenely as we may the consideration of the scientific problems with which we are confronted.

*Refining Gold Bullion.*

The problem presented by the necessity of refining gold was one for which a solution was sought at least as early as the time, about B.C. 700, when coins were first manufactured in the Western world. Apart from toughening or the removal of base metals, which was sufficiently cared for by the ancient process of cupellation, it is clear that some measure of success attended the efforts made to part gold and silver. Thus the coins of the Kings of Lydia (B.C. 687 to B.C. 500) and the primitive coinage of the cities of Iona (seventh and sixth centuries B.C.) show that pure gold and electrum were coined side by side at that time as distinct metals, having different monetary values, between which there was no confusion (Lenormant, "La Monnaie dans l'antiquité," 1878, i., 194). The gold leaf from the Egyptian mummies of the Persian era (B.C. 527 to B.C. 420) was 998 fine (W. Gowland, "The Metals in Antiquity," Huxley Memorial Lecture for 1912, *Journ. Royal Anthropol. Inst.*, 1912, xlii., 253). The gold staters of Greece were of varying degrees of fineness, the purest being those of Philip of Macedon, B.C. 350, some of which contained 997 parts of gold and 3 of silver (Lenormant, "La Monnaie dans l'antiquité," 1878, i., 187). The gold of Augustus was 998 fine (*Op. cit.*, p. 201). It may be taken for granted that such gold was not found native.

There is little doubt that the earliest parting process was one of cementation, by which silver and other metals were gradually converted into chlorides at a red heat and removed from the gold by absorption into the cement. Parting by cementation held the field for many centuries, and only very slowly fell into disuse after the discovery of more rapid and effective methods. The nitric acid process, with some help from sulphur, antimony, &c., was predominant for five or six hundred years, but sulphuric acid has been in use in refining for only a century, and chlorine gas and electrolysis for less than fifty years. Compared with the long past of the older methods of metallurgy, the duration of modern methods seems to be little more than an episode (see Roberts-Austen, *Journ. Iron and Steel Inst.*, 1899, lv., 18).

The following table of the various processes of separating gold from silver, and the earliest references to them, partly follows Percy ("Silver and Gold," p. 356), Gowland ("Metals in Antiquity," Huxley Memorial Lecture for 1912, *Journ. Royal Anthropol. Inst.*, 1912, xlii., 252), and Hoover (Translation of Agricola, "De re Metallica," 1912, footnote p. 458; Appendix B, p. 607).

TABLE I.

1. Cementation with salt. Agatharcides, about 113 B.C. (Gowland, *loc. cit.*; see also Freise, "Geschichte der Bergbau und Hüttentechnik," Berlin, 1908, i., 103; Beck, "Geschichte des Eisens," i., 74); ? Strabo, B.C. 63—A.D. 24; Pliny, A.D. 23/79.
2. Melting with sulphur. Theophilus, 11th century; at later dates additions of copper or iron were made.
3. Boiling in nitric acid. Geber or Albertus Magnus, 13th century.
4. Melting with antimony sulphide. Basil Valentine, end of 15th century, or *Probierebüchlein*, beginning of 16th century. Copper was sometimes added.
5. Cementation with nitre. Agricola, 1556.
6. Boiling in sulphuric acid. Earliest reference, Scheffer, 1753; applied by D'Arcet in 1802.
7. Passing chlorine gas through the molten metal. Earliest reference, Thompson, 1838; applied by Miller in 1869.
8. Dissolving in *aqua regia*, brought forward by Pettenkofer in 1847 (*Dingler's Polytechn. Journ.*, 1847, civ., 118 and 198; Borchers's "Electric Smelting and Refining," Eng. trans. 2nd ed., 1904, p. 359).
9. Electrolysis. Watt, 1863; applied by Wohlwill in 1878.
10. Boiling successively in nitric and sulphuric acids. Introduced by Mason in 1866 ("Production of the Precious Metals in the United States," 1885, p. 278).

Of these the only ones now in continuous use on a large scale are the sulphuric acid, chlorine gas, and electrolytic processes. The amount of gold annually refined is about £10,000,000 by chlorine gas, over £15,000,000 by electrolysis, and, say, £70,000,000 by sulphuric acid.

The obsolete processes have been described once for all by Percy, and there is little that is new to be said about the sulphuric acid and chlorine gas processes. The recovery of bluestone by crystallisation is now becoming obsolete, as it appears to be more profitable in general to recover the copper by electro-deposition. The sulphuric acid thus regenerated is concentrated, so that both the copper and the sulphuric acid can be used over again.

*Preliminary Toughening of Bullion.*

Where cupellation is not practised the preliminary removal of base metals or "toughening" of bullion is still effected by the old saltpetre process in some places; in others the ancient method of directing a blast of air on the surface of the molten metal and slagging off the oxides with borax has been reintroduced. In some chlorine refineries oxygen is passed through molten metal of low grade to toughen it and to enable the bullion to be correctly valued before the silver is separated from the gold by the passage or chlorine. It is satisfactory to be able to record that this advance is directly due to a paper read before our Institution (*Trans. I.M.M.*, 1905, xiv., 378).

The use of manganese dioxide or permanganate of potash instead of saltpetre has not yet been adopted by the ordinary refineries, and is, perhaps, not needed by them. An interesting application of these agents was made by Dr. W. A. Caldecott last year, when he was called on at short notice to refine gold bullion in the Transvaal so as to render it fit for coinage, a measure which was rendered necessary by the outbreak of the war. One of the difficulties was that Transvaal gold is only about 860 fine in gold, and therefore considerably below standard, and that the alloying metal is chiefly silver. Dr. Caldecott's first attempts were made by fusing granulated mill gold with potassium permanganate,  $\text{KMnO}_4$ , but the process of carrying silver into the slag was too slow, owing to the comparatively small surface of the metal granules, and success was finally attained by using the finely divided acid-treated calcined gold-zinc slime. Any lumps formed during calcination were broken up, and the

\* Presidential Address, delivered before the Institution of Mining and Metallurgy, March 18, 1915.

slime was left in the furnace until it was thoroughly burnt. The following charge was then prepared for fusion:—

	Parts.
Calcined gold slime .. .. .	100
Manganese dioxide .. .. .	30
Sand .. .. .	30
Borax (calcined) .. .. .	30

After fusion the charge was poured into conical moulds and the resulting buttons were granulated and fused with 20 per cent of permanganate of potash, together with some sand and borax, in order to remove any residual traces of zinc, lead, &c. Preliminary trials made in this way yielded over 4000 ozs. of bullion, containing between 926 and 952 parts of fine gold per 1000, with an average composition of:—

	Parts.
Gold .. .. .	938
Silver .. .. .	55
Base metal (probably copper) .. .. .	7
	1000

The refined metal could be alloyed with copper to make bars of standard fineness, and these proved to be perfectly malleable and ductile and suitable in all respects for coinage. Although no coins were actually struck, the anticipated need not having arisen, an expression of thanks was conveyed from the Union Government to Dr. Caldecott and to the Consolidated Goldfields Company in respect of the work. In congratulating Dr. Caldecott on thus rising to the occasion, it is permissible to express a doubt whether his achievement will encourage the use of such dangerous reagents in the ordinary toughening of bullion (for reference to prior use of  $MnO_2$  and  $KMnO_4$ , see E. H. Johnson and W. A. Caldecott, *J. C. M. and M. Soc. of S.A.*, 1902, iii., p. 46; W. Dowling, *op. cit.*, 1905, v., 224, and 1907, vii., 212).

#### Refining by Electrolysis.

The electrolytic process of repuration consists of two distinct operations, the silver nitrate process for alloys containing large proportions of silver, and the gold chloride process for alloys consisting principally of gold. The latter was brought forward by Dr. Wohlwill, of Hamburg, in 1874 (*Electro-Chem. and Met. Ind.*, 1904, ii., 221), and the former by Moebius in 1884. Both have been elaborated in the United States Mints since 1902 by Dr. D. K. Tuttle and others, but, so far as their essential features were concerned, both were described by an Englishman several years before anything was heard of them even in Germany.

The description was given in 1863 by Charles Watt, of Sydney, in a communication now in my possession, which was addressed to Thomas Graham, at that time the Master of the Mint, London. References were made to it in the Australian newspapers. Watt used a solution to which he added from "one-fourth to one-fifth its bulk of hydrochloric acid" (or, say, 8 per cent of HCl). This he "carefully added" until bubbles of chlorine ceased to be evolved from the anode. He does not mention the heating of the solution nor the occasional addition of chloride of gold to the bath. Heating, however, would not be necessary under the conditions which he gives, and he gave a full account of the preparation of chloride of gold by electrolysis without the aid of aqua regia which was unknown to Wohlwill, but was rediscovered by R. L. Whitehead at the Denver Mint in 1906 and described in 1908 (*Electro-Chem. and Met. Ind.*, Sept., 1908, p. 357).

The original solution, according to Watt, was to contain 0.5 oz. of gold per pint, or 27 grms. per litre, approximately the same strength as that recommended by Wohlwill. It is remarkable how little Wohlwill has advanced beyond Watt. The voltage used was 1.7, and anodes one-tenth of an inch thick were dissolved in twenty-four hours. The rate of dissolution corresponds to a

current density of 400 amperes per sq. m., or about the same as that used in Germany. The silver chloride was brushed from the anodes if necessary.

Graham submitted the proposal to George Gore, the well-known authority on electrolysis. Gore wrote in terms of approval of the process, and Graham referred it back to the Sydney Mint, but it was not adopted, on the alleged ground that no parting process was necessary there. The chlorine process was afterwards introduced at Sydney in 1869.

Watt also described in 1863 the electrolytic parting of gold-silver alloys "containing not less than three parts of silver to one part of gold" in a nitric acid solution, thus antedating by many years the Moebius process and its application in the United States Mints to such alloys. Watt stated that he was negotiating "for the introduction of his process in Europe, and may have unintentionally supplied the ideas used in the later patented processes of the Germans Moebius and Wohlwill. Watt did not patent his process and it was speedily forgotten.

It is interesting to recall that in 1851, before he left England, Charles Watt took out a patent for preparing caustic soda and chlorine by the electrolysis of a solution of common salt, a process which remained undeveloped for forty years. The fact is that he was a little before his time. If the dynamo had made its appearance before his various proposals were brought forward instead of afterwards (in 1867) he might have obtained a hearing.

In 1874 E. Wohlwill began experiments in Hamburg with the object of separating gold from platinum (*Electro-Chem. and Met. Ind.*, 1904, ii., 221). The gold chloride process bearing his name has been in use at the Norddeutsche Affinerie, Hamburg, since 1878, and in 1881 the products were shown at the Electrical Exposition at Paris. Later it was introduced at Frankfurt, at Freiburg-Halsbrücke, at Petrograd, and in 1912 at the Imperial Mints of Austria.

The electrolytic process was worked out independently at the Philadelphia Mint in 1898-1902 (Report of the Director of the United States Mint, 1902, p. 122), and during the last few years has been used for refining at the United States Mints, superseding the nitric and sulphuric acid processes. It has also been adopted at the new Mint at Ottawa. Descriptions of the method have been published from time to time (*Op. cit.*, 1906, p. 57), and I do not propose to describe it fully here, but there are certain points of interest to which I will direct your attention. I confine my remarks to the gold chloride, or Wohlwill process.

(To be continued).

## THE ELECTRO-TITRAMETRIC METHOD AND ITS APPLICATION TO GENERAL ANALYTICAL CHEMISTRY.\*

By F. H. HESSELINK VAN SUCHTELEN and ARAO ITANO.

(Concluded from p. 176).

In the experiments now to be described, determinations were made of several cations. The first was that of K in KCl (Sylvia). The reagent used here was sodium cobalt nitrite. The result obtained was once more in exact accord with the theoretical calculation: actually present, 39.10 mgrms. determined by the conductivity titration, 39.10 mgrms. (Fig. 9).

In this case the precipitation requires three to four minutes for completion. The conductivity reading then becomes constant. Although the conductivity curve in this instance permits of reasonably high accuracy, it is nevertheless not as sharp as in the other determinations which preceded, or in those which follow it. We have,

\* From the *Journal of the American Chemical Society*, xxvii, No 9

however, good grounds for the belief that by the use of another cobalt nitrite a sharper graph would result; in any case the reagent must be used fresh.

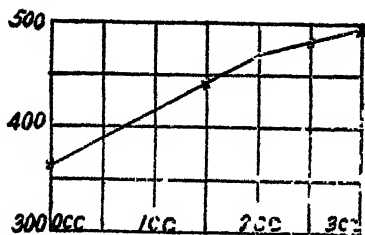


FIG. 9. - Determination of K.

In cup 10 cc. 0.1 N KCl.

Titrated with 0.5 N  $\text{Na}_2\text{CO}_3(\text{NO}_2)_6$

	Readings.
0 cc. . . . .	362.5
1.5 cc. . . . .	412
2.5 cc. . . . .	482
3.0 cc. . . . .	495.5

Theoretically, 2 cc. = 39.10 mgrms. K. Found, 2 cc. = 39.10 mgrms. K.

The next determination of a cation was that of Ca in  $\text{CaCl}_2$  (Fig. 10). The reagent used was 0.5 N oxalic acid. As before the result of the analysis checked with the theoretical amount present.

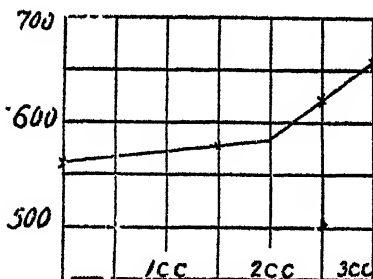


FIG. 10. - Determination of Ca.

In cup 10 cc. 0.1 N  $\text{CaCl}_2$ .

Titrated with 0.5 N  $\text{H}_2\text{C}_2\text{O}_4$ .

	Readings.
0 cc. . . . .	562.5
1.5 cc. . . . .	578.0
2.5 cc. . . . .	623.5
3.0 cc. . . . .	657.5

Theoretically, 2 cc. = 20.035 mgrms. Ca. Found, 2 cc. = 20.035 mgrms. Ca.

The next experiment was the determination of the  $\text{Fe}''$  content of  $\text{FeCl}_2$  (Fig. 11). The titration was performed with 0.5 N  $\text{Na}_2\text{S}$ . One can hardly fail to be struck here with the extraordinary sensitivity of the electro-titrametric method so notably illustrated by the results of this experiment. Thus, 2.792 mgrms.  $\text{Fe}''$  was dissolved in the conductivity cup. A glance at the graph shows that by the analysis exactly this amount was found to be present.

Up to now we have considered exclusively the analysis of elements and radicles in a solution containing only the pure salt. It is hardly necessary to say that by the application of such reliable and specific reagents as we used, the accuracy of the results would not be affected by the presence of foreign substances. Many experiments have convinced us of the applicability of the electro-titrametric method in the case of a solution of a mixture of salts. We invariably found that the presence of salts

other than the one in question did not cause variation or inaccuracy of results. For this reason we feel it unnecessary to go any further into this question, resting content with the statement that intelligent choice of the reagents used will, in the case of a mixture of substances in solution, prevent the possibility of even the slightest disturbance. A single illustration of this may be seen in Fig. 12, representing the determination of four different substances, Ag, Cl, Ba,  $\text{SO}_4$ , in a solution containing a mixture of  $\text{K}_2\text{SO}_4$  and  $\text{NaCl}$ . The graph speaks for itself in language that is unmistakable.

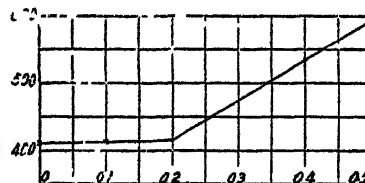


FIG. 11. - Determination of  $\text{Fe}''$ .

In cup 1 cc. 0.1 N  $\text{FeCl}_2$ .

Titrated with 0.5 N  $\text{Na}_2\text{S}$ .

	Readings.
0 cc. . . . .	410
0.1 cc. . . . .	410.7
0.4 cc. . . . .	535
0.5 cc. . . . .	594

Theoretically, 0.2 cc. = 2.792 mgrms.  $\text{Fe}''$ . Found 0.2 cc. = 2.792 mgrms.  $\text{Fe}''$ .

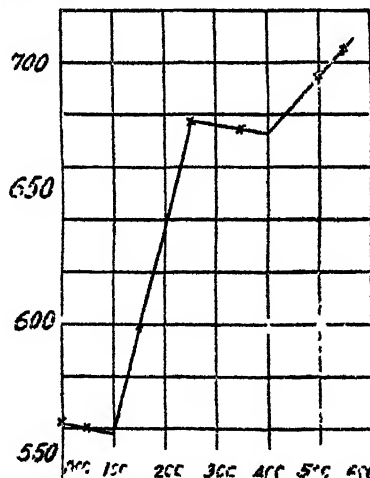


FIG. 12. - Determination of Cl and  $\text{SO}_4$  in the same solution.

In cup 5 cc. 0.1 N  $\text{NaCl}$ ; 5 cc. 0.1 N  $\text{K}_2\text{SO}_4$ .

Titrated with (A) 0.5 N  $\text{AgNO}_3$ ; (B)  $\text{N}/3 \text{ Ba}(\text{NO}_3)_2$ .

	Readings.
A.	
0 cc. . . . .	563.0
0.5 cc. . . . .	560.5
1.5 cc. . . . .	598.5
2.5 cc. . . . .	678.0
B.	
0 cc. . . . .	678.0
1.0 cc. . . . .	675.0
2.5 cc. . . . .	694.5
3.0 cc. . . . .	706.0

A - Theoretically, 1 cc. = 35.46 mgrms. Cl. Found, 1 cc. = 35.46 mgrms. Cl.

B. - Theoretically, 1.51 cc. = 96.09 mgrms.  $\text{SO}_4$ . Found, 1.5 cc. = 96.09 mgrms.  $\text{SO}_4$ .

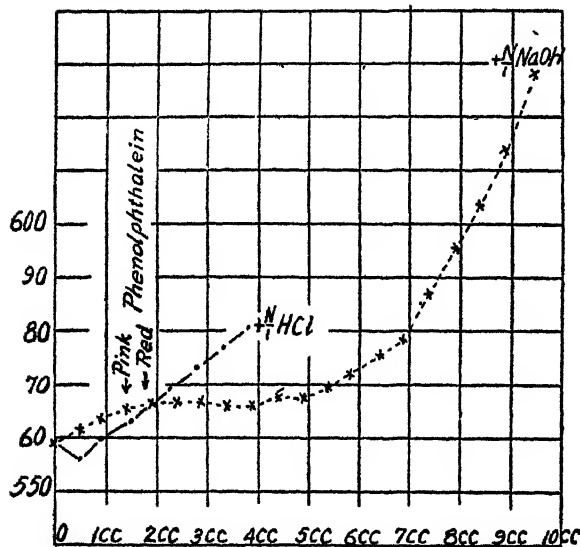


FIG. 13.—Determination of the acids and basic binding capacity (HCl, NaOH) of urine (sp. cond. 260°510-4).

In cup 50 cc. urine

Titrated with (A) N HCl; (B) N NaOH.

Acid Binding (A).					Readings.
0 cc.	..	..	..	..	555°0
0·5 cc.	..	..	..	..	556°5
0·9 cc.	..	..	..	..	560°0
1·5 cc.	..	..	..	..	563°5
2·3 cc.	..	..	..	..	569°5
2·8 cc.	..	..	..	..	573°5
3·3 cc.	..	..	..	..	577°0
3·8 cc.	..	..	..	..	580°7

Base Binding (B).					Readings.
0 cc.	..	..	..	..	559°0
0·5 cc.	..	..	..	..	561°5
0·9 cc.	..	..	..	..	564°0
1·4 cc.	..	..	..	..	565°5
1·9 cc.	..	..	..	..	566°5
2·4 cc.	..	..	..	..	567°0
2·9 cc.	..	..	..	..	567°0
3·4 cc.	..	..	..	..	566°0
3·9 cc.	..	..	..	..	566°0
4·4 cc.	..	..	..	..	567°5
4·9 cc.	..	..	..	..	567°5
5·4 cc.	..	..	..	..	569°5
5·9 cc.	..	..	..	..	572°0
6·4 cc.	..	..	..	..	575°5
6·9 cc.	..	..	..	..	581°0
7·4 cc.	..	..	..	..	587°0
7·9 cc.	..	..	..	..	595°5
8·4 cc.	..	..	..	..	603°5
8·9 cc.	..	..	..	..	614°0
9·4 cc.	..	..	..	..	628°0

Previously, we dealt with the determination of acids, bases, salts, and mixtures of salts. At this point we take occasion to state that this method, which was so successful for the above mentioned substances, was also of great value in the analysis of liquids of biological constitution. We have purposely concentrated the largest part of our attention upon the analysis of the working basis of the method in its wider applications. Therefore we reserve, for later publication, the analysis of biological liquids. We may, however, remark that by means of our method of analysis of the chlorine and phosphate in such liquids

(for example, urine) no difficulties were presented, the results being in perfect accord with those obtained by the other methods. The advantages of the electro-titrametric method in these latter instances are the possibility of an exact analysis of a few cc., and at the same time an extremely high degree of precision.

It is necessary here to call attention to the fact that in the determination of  $\text{SO}_4$  in such liquids certain complications were encountered, which impressed us with the fact that we had to deal with a liquid of different composition from the synthetical solution. Observing certain precautions, as, for example, degree of acidity, kind of reagent, &c., we were in some instances able to obtain results which closely agreed with those of gravimetric determinations.

The last curve (Fig. 13) is an illustration of the acid- and base-binding capacity of a physiological liquid, in this case urine. The previous statement in regard to the use of indicator is especially true in this case. It should not be overlooked, however, that the direction of the curve in such cases is probably not entirely due to the above stated phenomena, because other factors, such as changing viscosity, may affect the total result. It is interesting to note that in this connection successive precipitations were observed after the addition of certain amounts of the reagent.

It is the belief of the writers that such curves may prove to be in some cases a more instructive demonstration of the complex properties of such liquids, and that more deductions might be drawn from such curves than those from a turning point of an indicator.

As the nature of this publication is preliminary, the authors wish to reserve the right to develop this field more completely in the near future.

## THE NITROGEN OF PROCESSED FERTILISERS.\*

By ELBERT C. LATHROP,  
Scientist in Soil Fertility Investigations.

(Concluded from p. 107).

### THE CHEMICAL PRINCIPLES UNDERLYING THE UTILISATION OF NITROGENOUS TRADE WASTES.

In these days of conservation and scientific management more and more attention is being paid to the trade wastes from the various industries, and to the municipal scrap heaps. Things which were formerly thrown away are now often made to pay for the entire cost of production. After the resources of the chemist and inventor have failed in finding any other use for some industrial waste, if it be of a nitrogenous nature, the fertiliser industry is turned to as a last resort. Here, however, all is not plain sailing, since many of these nitrogenous substances are of such a nature that the nitrogen is said to be "unavailable" for plant use—that is, the substance is of such a nature that it is not readily decomposed by the natural agencies at work in the soil, so that for the purpose of plant nutrition the nitrogen of such substances is worthless or of little value. In order to render available this type of nitrogenous material many different kinds of treatment have been suggested, and the patent literature abounds in inventions of this sort.

It has already been stated that in order that the plant may make use of the nitrogen of even high-grade organic fertilisers it is necessary for the proteins therein to be at least partially decomposable by the biological and biochemical agencies of the soil. The low-grade organic nitrogenous fertilisers resist decomposition by these biological and biochemical soil agencies, and their nitrogen is therefore considered to be less available for plant use.

\* Bulletin No. 158, United States Department of Agriculture Bureau of Soils.



The guiding idea behind the processes proposed for the treatment of trade wastes which will not decompose easily in the soil as such is to change the nitrogen compounds contained in them in such a way that ammonia is formed, and that their decay in the soil is more rapid.

Much of the nitrogenous materials in trade wastes is of a protein nature, since the products from which these wastes are derived are either of animal or vegetable origin. Such is the case with the wastes used in the manufacture of base goods. It has been shown that by the process used in the case of this fertiliser the non-available nitrogenous materials have been made highly available, not only because the nitrogen compounds can be ammonified quickly in the soil, but also because these compounds are directly utilisable by plants. This change in the nature of the nitrogen compounds has been brought about by the partial hydrolysis of the proteins contained in the various trade wastes used in the manufacture of the fertiliser. When proteins decompose through natural conditions, be they in the soil or out of it, a certain amount of hydrolysis of the proteins takes place, and if the decomposition is allowed to proceed long enough under proper conditions complete hydrolysis will result.

The principle involved in making the nitrogenous material in the soil available and in increasing the availability of low-grade nitrogenous materials by factory treatment is therefore the same. In other words, the general chemical principle to be applied in making available the nitrogen of low-grade fertilisers, trade wastes, &c., is that of complete or partial hydrolysis by any suitable means of the proteins contained in the wastes. Partial hydrolysis of proteins may be accomplished by means of heat, boiling, steaming, heating under pressure, and both partial and complete hydrolysis may be obtained by treating with strong acids or alkalis, either in the cold for a long time or heating to a high temperature, the extent of hydrolysis depending on the several conditions. In a number of processes already in use various of these treatments are practised, resulting in different degrees of hydrolysis of the original proteins. While the availability of the nitrogen of a fertiliser depends on the substances in which the nitrogen is contained, it also depends on the extent of hydrolysis of the proteins used in the manufacture. It may be stated that in general the more extended and final the hydrolysis the more available the nitrogen of the compounds formed, since, as has been shown, the final products of hydrolysis are utilised by the plant as such, and are at the same time more readily changed into ammonia by bacteria, &c., than are the intermediate compounds produced by partial hydrolysis.

#### SUMMARY.

The base goods used as a type of processed fertilisers is an organic nitrogenous fertiliser which contains acid phosphate. This product is produced by the action of sulphuric acid on certain trade wastes; the heat is generated by the interaction of the acid with the organic wastes and rock phosphate in the course of the manufacture of acid phosphate. It is here shown that the hydrolysis of the protein is almost complete, the nitrogenous compounds in the finished fertiliser being principally the products of primary protein decomposition, together with a small amount of proteose-like compound which has persisted.

From the sample of base goods were isolated the following nitrogenous compounds—two purine bases, guanine and hypoxanthine; the three diamino acids, arginine, histidine, and lysine; and two monoamino acids, leucine and tyrosine. A proteose-like compound was also obtained and its general nature established.

By means of the Van Slyke method the approximate proportions of the different forms of nitrogen contained in the fertiliser were estimated, and the extent of the hydrolysis of the original proteins was determined. It was also shown by this method that the proteose-like compound was composed of acid amide radicles, diamino acid radicles, especially lysine, and monoamino acid radicles,

particularly the monoamino acids which contain non-amino nitrogen.

The question of the availability of nitrogen is discussed, and from a consideration of the amount and the physiological action on plants of the different forms of nitrogen present in the fertiliser it is concluded that the water soluble nitrogen of this fertiliser should have an availability equal to or greater than the nitrogen of dried blood or other high-grade fertilisers. These results are in accord with the results obtained by the plant method of determining availability.

The general chemical principle which underlies the method for rendering available the nitrogen contained in most trade wastes which are to be used as fertilising materials is shown to be either partial or complete hydrolysis of the protein of the wastes by any suitable means.

The more complete the hydrolysis the more available the nitrogen in the fertiliser becomes, since the products of complete hydrolysis of proteins are not only utilised by the plants themselves as nutrients, but they are more easily ammonified when placed in the soil than are the more complex compounds, such as peptones, proteoses, and the proteins themselves.

This investigation aims only at an explanation and exposition of the general chemical principles involved in the treatment of trade wastes and other organic material to render the nitrogen contained therein more available for agricultural purposes. It does not aim to present the research methods here employed as general methods for analysing such fertilisers, nor can the quantitative figures obtained be expected to apply to all products of similar manufacture, for the reason that the different kinds of nitrogen compounds will necessarily show different proportions according to the nature of the materials which enter into the mixture.

#### GLASS RESEARCH,

THE Council of the Institute of Chemistry of Great Britain and Ireland appointed a Glass Research Committee in October last to conduct investigations with a view to arriving at suitable formulæ for laboratory glass-ware, miners' lamp glasses, combustion tubing, resistant glass for pharmaceutical products, glass for X-ray bulbs, &c.

The Council have published a short report summarising the work of this Committee with a view to arriving at suitable formulæ to be freely available to manufacturers willing to assist in maintaining the continued supply of laboratory glass ware. The importance of this work to numerous industries, particularly those concerned with the production of war material, will be apparent.

The Committee consisted of Prof. Raphael Meldola (then President of the Institute), Mr. Bertram Blount, Mr. Otto Hehner, Prof. Herbert Jackson, Mr. Walter C. Hancock, and Mr. T. R. Merton. At their first meeting Prof. Herbert Jackson reported that, in conjunction with Mr. T. R. Merton, he had already commenced experiments at King's College, London, with a similar object in view, and that he and his collaborator were prepared to give the Committee the results of their work up to that date, and to pursue investigations on lines to be determined from time to time by the Committee.

Since then, the research has been continued uninterruptedly, the chief aims being:—(i.) To produce working formulæ for all glasses used in laboratory work, and (ii.) to ascertain the influence of various ingredients on the physical and chemical properties of glasses. The work was extended to include glass for miners' lamp glasses, at the suggestion of the Home Office, and also glass for ampoules, to meet the needs of wholesale pharmaceutical chemists engaged in the production of Army medical requirements. The Committee have also examined and reported on samples of British and French laboratory glassware, produced since the beginning of the war,

a number of the specimens being made from formulæ similar to, and in some cases almost identical with, those recommended by the Committee.

The Committee have had before them many specimens of glasses used for various purposes, of which analyses have been made by Mr. Blount, Mr. Hancock, and Mr. Hehner. It has been found, however, that mixtures prepared in accordance with the analytical results were not always satisfactory; but the analyses were helpful in suggesting synthetic experiments, and during recent investigations some intricate analyses made by Mr. Gilbert J. Alderton under the supervision of Mr. Blount have proved especially valuable. Apart from the analyses, the work has been almost entirely carried on at King's College by Prof. Jackson and Mr. Merton, and by the former at his own house. The work has involved a careful study of the chemistry of silicates, aluminates, borates, &c., in their relation to the manufacture of glasses. A detailed report of these experiments will be published in due course.

Up to the present time, the Research Committee have reported eleven formulæ for glasses for various purposes based on the results of about 400 experimental melts on a scale large enough for drawing rods and blowing small vessels. In addition, a very great number of experiments have been made in order to study the influence of the various constituents employed. No formula has been issued without submitting the specimens made to rigorous tests to prove their suitability for the purposes for which they are intended. Moreover, by varying the experimental working conditions, it can be said with reasonable confidence that the mixtures will prove equally satisfactory under the actual working conditions of a glass furnace. The question of workable temperatures has been carefully considered, and, so far as it is possible to judge, the melts on a small scale indicate that even better results will be obtained on the industrial scale. This view has been justified by the samples already received from manufacturers who have tried some of the formulæ.

In deciding the formulæ it has been found necessary to pay special attention to the proportions of basic and acidic substances in respect of the action of glass mixtures on clay crucibles during fusion, and it has been shown by careful investigation that the formulæ proposed give melts in which the influence of the ingredients of the crucibles is very slight, and in some cases practically inappreciable.

The following formulæ have been communicated to a number of manufacturers who have expressed their interest in the progress of the investigation and to scientific workers who are conducting similar experiments.

*Soft Glasses*, suitable for ordinary chemical laboratory ware :—

	Parts.
1. Sand.. ..	67.0
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	34.2
Calcium carbonate.. ..	11.6
Alumina, $\text{Al}_2\text{O}_3$ .. ..	6.5

A soft glass which does not give up alkali readily to water, works well in the blowpipe, and does not devitrify readily.

	Parts.
2. Sand.. ..	67.0
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	29.0
Calcium carbonate.. ..	9.6
Calcium fluoride .. ..	1.6
Alumina, $\text{Al}_2\text{O}_3$ .. ..	8.3
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	2.0

A soft glass of higher quality. Does not give up alkali under severe tests. A kindly working glass before the blowpipe, and very difficult to devitrify.

*A Resistant Glass* suitable for pharmaceutical purposes, ampoules, &c. :—

	Parts.
3. Sand.. ..	67.0
Alumina, $\text{Al}_2\text{O}_3$ .. ..	10.0
Calcium carbonate.. ..	12.5
Magnesia.. ..	0.5
Potassium nitrate .. ..	1.0
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	17.0
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	8.0

This glass is intermediate in hardness between soft glass and combustion tubing, is highly resistant to chemical action, withstands changes of temperature well, and should be a very suitable glass for high class beakers, flasks, &c.

*Glasses for Combustion Tubing* :—

	Parts.
4. Sand.. ..	68.2
Alumina, $\text{Al}_2\text{O}_3$ .. ..	6.2
Barium carbonate .. ..	8.8
Calcium carbonate.. ..	13.0
Potassium nitrate .. ..	4.3
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	5.5
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	5.5
Calcium fluoride .. ..	1.0

This glass resembles Jena combustion tubing very closely indeed. It has practically the same fusing-point. It fuses on to Jena glass perfectly, and is indistinguishable from it before the blowpipe and in its behaviour on prolonged heating below its fusing-point. The presence of the small quantity of calcium fluoride facilitates the incorporation of the ingredients. The sodium carbonate can be reduced to 1.34 parts provided 7.93 parts of anhydrous borax be used in the place of boric anhydride.

	Parts.
5. Sand.. ..	68.2
Alumina, $\text{Al}_2\text{O}_3$ .. ..	6.2
Barium carbonate .. ..	8.8
Calcium carbonate.. ..	14.2
Potassium nitrate .. ..	4.3
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	5.5
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	5.5

This glass is practically of the same composition as 4. It is not so easy to make or to work, but it does not become so opaque as Jena combustion tubing on prolonged heating. As in No. 4, the proportions given for sodium carbonate and anhydrous borax can be substituted for the figures for sodium carbonate and boric anhydride.

*Miners' Lamp Glasses* :—

	Parts.
6. Sand.. ..	65.0
Alumina, $\text{Al}_2\text{O}_3$ .. ..	1.0
Calcium carbonate.. ..	0.6
Arsenious oxide, $\text{As}_2\text{O}_3$ .. ..	2.0
Antimony oxide, $\text{Sb}_2\text{O}_3$ .. ..	1.0
Potassium nitrate .. ..	3.0
Sodium carbonate, $\text{Na}_2\text{CO}_3$ ..	14.0
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	24.0

A colourless and fusible glass withstanding rapid changes of temperature exceptionally well.

	Parts.
7. Sand.. ..	65.0
Alumina $\text{Al}_2\text{O}_3$ .. ..	1.0
Calcium carbonate.. ..	0.6
Arsenious oxide, $\text{As}_2\text{O}_3$ .. ..	2.0
Antimony oxide, $\text{Sb}_2\text{O}_3$ .. ..	1.0
Potassium nitrate .. ..	3.0
Anhydrous borax, $\text{Na}_2\text{B}_4\text{O}_7$ ..	26.68
Boric anhydride, $\text{B}_2\text{O}_3$ .. ..	5.5

The same glass as 6, but the ingredients have been varied to avoid the use of so much boric anhydride, which is at present apparently difficult to obtain on a commercial scale.

Resistance Glass :—

	Parts.
8. Sand, . . . . .	65.5
Alumina, $Al_2O_3$ . . . . .	2.5
Magnesia, $MgO$ . . . . .	5.0
Zinc oxide, $ZnO$ . . . . .	8.0
Sodium carbonate, $Na_2CO_3$ . . . . .	10.2
Borax anhydrous, $Na_2B_4O_7$ . . . . .	13.0

A glass almost identical in its general behaviour with Jena resistance glass; with stands changes of temperature well, but, like Jena, is not suitable for working before the blowpipe. It darkens and tends to devitrify; operations—such, for instance, as sealing side tubes into flasks are difficult, if permanent and neat joints are required.

Formula No. 3, recommended for pharmaceutical purposes, ampoules, &c., may be substituted for the resistance glass with advantage, as the ampoule glass lends itself very well to blowpipe work, and is also especially resistant chemically.

Alternative for Combustion Tubing :—

	Parts
9. Sand, . . . . .	72.0
Alumina, $Al_2O_3$ . . . . .	10.0
Calcium carbonate, . . . . .	11.0
Magnesia, $MgO$ . . . . .	0.5
Potassium nitrate, $KNO_3$ . . . . .	3.0
Sodium carbonate, $Na_2CO_3$ . . . . .	11.2
Borax anhydrous, $Na_2B_4O_7$ . . . . .	7.2

This glass is capable of withstanding high temperatures and rapid changes of temperature; works well before the blowpipe, and is free from the chief defect of Jena glass, namely, the readiness with which it becomes cloudy and finally quite opaque after prolonged use. By slight modifications of this formula, almost any degree of hardness can be obtained.

In Formulæ 8 and 9 substances such as magnesia,  $MgO$ , and zinc oxide,  $ZnO$ , can be added in the form of carbonates if the actual percentages of  $MgO$  and  $ZnO$  respectively present in the carbonates are known.

Soft Soda Glasses suitable for tubing and X ray bulbs :—

	Parts.
10. Sand, . . . . .	68.0
Alumina, $Al_2O_3$ . . . . .	4.0
Calcium carbonate, $CaCO_3$ . . . . .	12.8
Potassium nitrate, $KNO_3$ . . . . .	14.5
Sodium carbonate, $Na_2CO_3$ . . . . .	26.0
11. Sand, . . . . .	68.0
Alumina, $Al_2O_3$ . . . . .	4.0
Calcium carbonate, . . . . .	12.8
Potassium carbonate, $K_2CO_3$ . . . . .	10.0
Sodium carbonate, $Na_2CO_3$ . . . . .	26.0

These glasses do not lose their easy-working qualities after repeated heating and blowing, and are plastic over a long range of temperature. They require a temperature of at least  $1400^\circ$  to  $1500^\circ$  C. for complete incorporation of the ingredients in order to obtain that homogeneity which is necessary for resistance to rapid changes of temperature and ease of working before the blowpipe.

No. 10, containing potassium nitrate, is considered the better of the two, and is more easily incorporated.

The committee consider that the formulæ they have obtained and the work they have done on the various glasses justify them in the opinion that there is now information available for the manufacture of all the important glasses used in the laboratory and for industrial purposes, which have hitherto been mainly obtained from abroad.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 26, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER entitled "*The Change of Thermal Conductivity with Fusion*," by Prof. A. W. PORTER and Mr. F. SIMEON, was read by the former.

The change in question was determined for mercury and for sodium by finding the temperatures at different points of a cylinder of the metal contained in a glass tube. The ends of the cylinder were maintained at such temperatures that the metal was liquid half-way down its length, the remaining part being solid. The temperatures were taken by means of thermoelectric junctions inserted in narrow tubular depressions which had been formed in the glass tube by forcing a knitting-needle down into the locally heated glass. The ratio of the thermal conductivity for solid and liquid was estimated from the slope of tangents drawn to the temperature-curve on each side of the melting-point. The values of these ratios are of the same order as the ratio of the corresponding values of the electrical conductivities. The mean value for mercury is 3.91, and for sodium 1.31.

A summary list is given of other data concerned with fusion.

DISCUSSION.

Prof. O. W. RICHARDSON congratulated the authors on their satisfactory treatment of an important problem. The change of thermal conductivity with fusion had not, he believed, been attacked experimentally before. In listening to the reading of the paper one felt impressed by the small amount of effort, and the simplicity of the apparatus with which the authors had been able to solve what was generally regarded as a very difficult problem. This research, it was interesting to note, was one of the few of which the results agreed with the deductions from the elementary electronic theory.

Prof. F. G. DONNAN referred to the researches carried out at his suggestion by Dr. C. M. Stubbs on the radiation emitted by copper, silver, and gold at high temperatures. These experiments showed that there was a marked change in the distribution of energy throughout the visible spectrum when passing from solid to molten metal, and pointed to some change in the electronic structure, or in the inter-electronic forces occurring at the transition from solid to liquid. The complexity of the problem had, so far, prevented any mathematical treatment, but there appeared no doubt that results such as these, coupled with the discontinuities in thermal and electrical conductivity, would be of value in throwing light on the inner mechanism of the phenomenon of melting. Photometric measurements of the light radiated by polished plates of metals at high temperatures presented considerable difficulties owing to the tendency of the "flowed" surfaces to crystallise, but in spite of these difficulties Dr. Stubbs had clearly demonstrated the existence of an abrupt change in the radiation-spectrum on passing from solid to liquid in the case of certain metals.

Prof. PORTER, in reply, said that while isolated measurements of thermal conductivity of some substances above and below the melting-point had been made by previous workers, in no case that he was aware of had sufficient data been obtained from which to deduce the sudden change which takes place on fusion. He was cognisant of the work of Dr. Stubbs, but had always thought the nature of the surface was of such importance in radiation experiments as to make it difficult, on account of crystallisation and contamination of the surface at high temperatures, to obtain conclusive results. He had forgotten at the moment the degree of consistency obtained by Dr. Stubbs, but if the results were more or less in agreement they

would undoubtedly point to a change at the fusion-point in the radiation emitted by the substances.

A paper, entitled "*An Instrument for the Optical Delineation and Projection of Physical Curves such as Hysteresis, Resonance, and Characteristic Curves*," was read by Dr. J. A. FLEMING.

This instrument is designed for projecting on to a screen or photographing on a plate such curves as magnetic hysteresis, resonance, or characteristic curves which can be performed slowly, or are non-periodic or non-repetitive. It consists of a base board on which is fixed a thin wooden ring wound over with one layer in close turns of insulated Eureka wire. The insulation on the top surface is removed so as to expose the wire. At the centre of the ring there is a pivot which carries a radial arm the end of which rubs on the bare Eureka wire. The ends of the Eureka wire are connected to a battery of  $n$  cells and the middle point of the wire is connected to a terminal, and also the centre of the radial arm to another terminal. The arrangement forms a circular potentiometer so that any required fraction of the battery voltage can be produced in either direction between the last mentioned two terminals. On the same base there is a rectangular mirror slung on a longitudinal axis, which mirror is tilted by a thread wound round the shaft of the radial arm of the potentiometer. Hence, if a ray of light from a mirror magnetometer or galvanometer is reflected to the tilting mirror and thence on to another fixed mirror with its axis at right angles to that of the other, and thence to a screen, the spot of light will have two motions, one a horizontal one proportional to the displacement of the radial arm, and therefore to the P.D. of the two terminals, and another vertical motion proportional to the deflection of the galvanometer or magnetometer. If, then, we place behind the magnetometer a long coil having a long iron wire within it and send a current through this coil which is supplied from the potentiometer travelling terminals, the spot of light will be actuated by two motions, one a horizontal one proportional to the magnetising force, and the other a vertical one proportional to the central flux density in the iron. It will therefore describe a hysteresis curve when the radial arm is moved to and fro cyclically through a certain arc or angle. In the same manner the instrument can be used to delineate characteristic curves of wireless detectors or rectifiers or other devices. By using a rotating condenser of variable capacity in place of the circular potentiometer, the instrument can be used for delineating resonance curves of wireless telegraph plants.

#### DISCUSSION.

Prof. S. P. THOMPSON complimented the author on the simplicity and effectiveness of his apparatus in which, as was characteristic of Prof. Fleming's devices, were embodied the results of much careful thought and painstaking experiment. He himself had often felt the desirability of having an arrangement by which one could vary the magnitude of an electric current in such a way that it should be directly proportional to some movement in a straight line. He had thought out various potentiometers in this connection, but the difficulty with potentiometers was the small current obtainable from them which was a disadvantage in magnetic work. Prof. Fleming had surmounted the difficulty of straight line proportionality by working round an axle instead.

Mr. W. DUDDALL joined in congratulating the author on the wide utility of his instrument. He recalled that when delivering his first lecture on the oscillograph he had been confronted with the problem of projecting the motion of a spot of light in two co-ordinates on a screen, and had used a very similar arrangement to Prof. Fleming's. He also had a circular rheostat, but instead of a string connection to the mirror he had used a cam. This apparatus had worked very satisfactorily.

Prof. E. WILSON said the apparatus was undoubtedly admirable for demonstration purposes, and one naturally wondered what degree of precision would be possible with

it if applied to research. It appeared from the step and stair motion of the spot on the screen that the speed would be limited on account of the damping of the magnetometer or galvanometer employed.

Prof. S. W. J. SMITH described a method which he had found to be simple and effective for tracing hysteresis loops. An ingenious rheostat had been devised by Prof. Morris in which by the rotation of a handle two contacts are made to slide in opposite directions along a resistance which is connected directly across the battery. The voltage at the contacts varies continuously between  $\pm$  the whole P.D. of the battery, being zero when they are at the middle. This rheostat is mounted vertically, and a white card of suitable size is attached to one of the moving contacts from which the magnetising current is taken; then, if the magnetometer spot is focussed on the card and its position marked as the current is varied, the hysteresis loop is easily traced out. The Morris resistance satisfies some at least of the requirements mentioned by Prof. Thompson, though for the method he had described simpler rheostats of similar type could also be used.

Prof. MORRIS agreed that the question of getting a current which is proportional to some linear motion was a difficult one. Before arriving at the design of the rheostat mentioned by Dr. Smith he had tried various other types, including a circular one similar to Dr. Fleming's. The main point about his rheostat was the magnitude of the currents which could be taken from it. It would stand 20 amperes for a short time.

Mr. A. F. HALLIMOND pointed out that in taking the characteristic curve of a contact if the resistance of the potentiometer is comparable with that of the contact, the linear relation between the motion of the slides and the P.D. the contact is destroyed. In his instrument, to which Prof. Fleming had referred, and which he hoped to describe more fully at a future occasion, it was possible to make the connections so that the linear relation always held.

Prof. FLEMING, in reply, thanked the various speakers for their remarks, and said that he hoped to improve considerably on the apparatus, especially as regards the optical arrangements. When this had been done he thought it would be extremely accurate, and quite suitable for research work.

A paper, entitled "*The Stability of some Liquid Films*," by Dr. P. PHILLIPS and Mr. J. ROSE INNES, was read by the former.

The authors give a simple method of calculating the equilibrium form of a thin film which is a surface of revolution.

They then consider the stability for certain kinds of displacement of three classes of such films, viz., the sphere, the cylinder, and the catenoid. The mathematics used is quite elementary throughout and the treatment is rigorous.

#### DISCUSSION.

Prof. J. W. NICHOLSON thought the paper was of considerable interest not only to teachers, as suggested by the author, but to physicists in general. He admired the geometrical construction given and the simple way in which the stability or otherwise of a particular form was determined.

A Demonstration of the Green-flash of the Setting of an Artificial Sun was given before and after the meeting by Prof. A. W. PORTER and Mr. E. TALBOT PARIS.

A large disc of card, mounted so that it can be slowly rotated, has a hole, one inch in diameter, cut in it about two inches from the periphery. This is covered with red gelatin films, and is illuminated from behind so as to form an artificial sun. The front of the disc is covered with white Bristol board, and is moderately illuminated by a lamp in front. This sun is viewed through a rectangular aperture (four inches wide) in a blackened board, the lower edge of the aperture serving as the horizon. When the disc is rotated the artificial sun sets

and green after-images are obtained of characters varying according to the amount that the eye has been exposed to the bright sun. If the sun is not viewed until immediately before the complete setting the after-image represents simply the disappearing segment to which it is due.

The authors claim that this phenomenon is what is often described as the green-flash at sunset, though they are ready to admit that other (but probably rarer) phenomena also go under the same name.

Mr. W. DUDELL proposed a vote of thanks to Profs. Fleming and Porter for their kind invitation to University College, and for the excellent programme which they had submitted to the Society.

The vote was unanimously endorsed by the meeting.

# SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 31, 1915.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

MESSRS. Christopher William McHugo, Cyril Joseph Heath Stock, George Tate, and Thomas Edward Wallis were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Edward Theodore Brewis, 31, Belgrave Road, Leyton, Essex; William McDonnell Mackey, Victoria Chambers, Leeds; and Percival John Fryer, Ravenscar, Pembury Road, Tonbridge, Kent.

The following papers were read:—

*"Estimation of Methyl Alcohol in presence of Ethyl Alcohol."* By G. CECIL JONES.

Simmonds (*Analyst*, 1912, xxxvii., 16) has confirmed the great delicacy of Denigès' method, which depends on oxidation of methyl alcohol by permanganate and colorimetric estimation of the formaldehyde produced, under conditions such that no ethyl alcohol can be oxidised to formaldehyde, and that acetaldehyde can develop no colour with the Schiff's reagent used for the colorimetric estimation of the formaldehyde. With one exception he has laid down conditions for the test which ensure a maximum of sensitiveness without risk of ambiguity in the results. He did not, however, show how serious were the errors which might attend a very small departure from some of the conditions he laid down. These are now shown, as well as the fact that the composition of the so-called Schiff's solution—not defined either by Denigès or Simmonds—is of the utmost importance, the formulæ to be found in many text-books yielding a solution quite useless for the purpose, unless some of the conditions laid down by Denigès and Simmonds are modified to meet the case. The accuracy and convenience of the method, under standard conditions easily realised, is confirmed.

*"Determination of Niobium in the presence of Tantalum, and some Reactions of Tantalum Compounds."* By ARTHUR G. LEVY.

A volumetric method for the determination of niobium in the presence of tantalum is described. The method is based on the fluoride method of Osborne, but reduction only goes as far as an oxide, Nb<sub>2</sub>O<sub>7</sub>, with an N/10 permanganate equivalent of 0.00834 grm. per cc.

It is shown that large losses of tantalum are caused by (a) dissolving tantalum oxide in hydrofluoric acid and igniting the residue obtained on evaporation to dryness, (b) igniting potassium tantalum fluoride with excess of potassium fluoride at a red heat, and (c) igniting mixtures of tantalum oxide and ammonium fluoride.

*"Estimation of CO<sub>2</sub> in Self-raising Flour and Baking Powders."* By THOMAS MACARA.

The author points out that the estimation of available CO<sub>2</sub> in baking powders, &c., by means of the Schrödter apparatus and similar methods does not include the CO<sub>2</sub> liberated by the action of heat on the excess of bicarbonate

generally present in these mixtures, and shows that bicarbonate of soda boiled for thirty minutes decomposes into the sesquicarbonate, thus liberating 25 per cent of its CO<sub>2</sub>. He further describes a simple method for estimating available CO<sub>2</sub> in such mixtures which will include this fraction.

*"Method for the Determination of Chlorine in Cheese."* By ELPREIDA C. V. CORNISH and J. GOLDING. (From the Dairy Research Department, University College, Reading).

The determination of the percentage of chlorine in cheese by the method of ashing is very tedious and unsatisfactory. A method has been devised by the authors to obviate this difficulty, and consists essentially of the distillation of chlorine from the cheese in the form of HCl by heating with strong H<sub>2</sub>SO<sub>4</sub> in a Kjeldahl flask, the precipitation of AgCl by the HCl so driven off, in a solution of AgNO<sub>3</sub> and concentrated HNO<sub>3</sub>, filtration of AgCl precipitate, and titration of unused AgNO<sub>3</sub> by Volhard's method. A further advantage of the method lies in the fact that the residual substance in the Kjeldahl flask can be used for nitrogen determination in the usual way.

*"Bromine Method of Determining Phenol."* By W. VERSFELD.

The author compares the value of sodium hypobromite solution, and of bromine in potassium bromide solution for estimating phenol, and finds that there is little to choose between them provided proper precautions are observed. He also gives figures which indicate that aqueous solutions of phenol slowly change on keeping, giving a higher "bromine value" than when freshly prepared.

*"Estimation of Sulphide and Sulphate Sulphur and the Action of Solvents on Vulcanised Rubber."* By HENRY P. STEVENS.

The vulcanised rubber is first swollen in a solvent such as ether, in which state sulphides, such as lead sulphide, are completely attacked by hydrochloric acid, and the sulphuretted hydrogen available may be collected and estimated, giving the sulphide sulphur present. The sulphate sulphur is contained in the acid extracts.

Tables are also given showing the progressive decomposition of vulcanised rubber by the action of acid in the presence of a solvent.

## THE BIOCHEMICAL SOCIETY.

THE next meeting will be a joint meeting of the Biochemical Society and the Society of Public Analysts and other Analytical Chemists, and will be held in the rooms of the Chemical Society, Burlington House, Piccadilly, W., on Wednesday, May 5th, 1915, at 8 p.m.

The meeting is to be devoted to a discussion of "Methods adopted in the Estimation of the Nitrogenous Constituents of Extracts derived from Albuminous Substances such as Meat Extracts and similar products, with special reference to the Interpretation of Results."

The following scheme, which represents the chemical methods commonly made use of in the examination of nitrogenous extracts, is intended to serve as the basis of discussion:—

*Meat Fibre and Coagulable Albumenoids.*—10 grms. of the extract are dissolved in 100 cc. of cold water. Five drops of acetic acid are added and the solution brought to the boil, and allowed to boil gently for five minutes. It is then filtered, and the precipitate is washed with warm water, and the nitrogen determined by Kjeldahl's method in the ordinary way. N × 6.25 = meat fibre and coagulable albumenoids.

*Albumoses and Peptones.*—The filtrate from the meat fibre and coagulable albumenoids is made up to a definite volume and an amount corresponding with 5 grms. of the original extract pipetted out. To this is added a few drops of hydrochloric acid, and then bromine water in large excess. The precipitate is then collected in tubes by means of a centrifugal machine, washed with bromine water in



the same way, dissolved in hot water, and Kjeldahled.  $N \times 6.25$  = albumoses and peptones. Some analysts are in the habit of saturating the filtrate from the coagulable albumenoids with zinc sulphate for the purpose of precipitating the albumoses. In that case the nitrogen so obtained is deducted from the nitrogen contained in the bromine precipitate, and the residue is calculated as peptone. It will be interesting to have the views of the meeting as to whether this particular separation has any practical utility. When gelatin is present this is also precipitated by the bromine, and the amount as determined below will obviously have to be subtracted from the total precipitate in order to arrive at the percentage of albumoses and peptones.

**Gelatin.**—5 to 20 grms. are dissolved in hot water and evaporated to dryness with sand. The dried mass is then ground finely in a mortar, placed in a beaker, and washed four times with ice-cold alcohol, about 50 cc. alcohol being used for each washing. The alcohol is pumped through an asbestos filter surrounded with ice. The sand is then extracted several times with ice-cold alcohol and water, gradually decreasing the strength of the alcohol with each extraction until the final washing solution contains only 10 per cent of alcohol by weight. In all about five-six washings of about 50 cc. each are required. The gelatin in the beaker and on the asbestos filter is then dissolved in boiling water and the nitrogen determined in the usual manner.  $N \times 5.44$  = gelatin.

**Creatine and Creatinine.**—A 10 per cent solution of the extract in distilled water is first prepared. Several 10 cc. quantities of this solution, representing 1 gm. of extract, are pipetted into small beakers, and to each 10 cc. of normal hydrochloric acid are added; the beakers are placed in an autoclave and heated for half an hour at a temperature of  $120^\circ\text{C}$ .; the whole of the creatine present is thus converted into creatinine. The conversion may also be carried out by dissolving 10 grms. of the extract in a 100 cc. flask in about 90 cc. of one-third normal HCl, heating in a boiling water-bath for four hours, allowing to cool, and making up to 100 cc. 10 cc. of this converted solution, representing 1 gm. of extract, are used for each colour experiment. 50 mgrms. of pure crystallised creatine (which contains one molecule of water of crystallisation) are similarly converted with hydrochloric acid and the solution made up to 100 cc. To the contents of one of the beakers, or to the solution of 1 gm. of extract otherwise converted, cooled to  $20^\circ\text{C}$ ., 30 cc. of a saturated picric acid solution and 15 cc. of a 10 per cent NaOH solution are added. After standing for five minutes the coloured liquid is made up to 500 cc. The colour is matched in any suitable colorimeter against that given by the standard creatinine solution. It can also be matched against 8 mm. of a solution of potassium bichromate containing 24.54 grms. of bichromate per litre, the colour of which corresponds with 10 mm. of creatine in 500 cc. of liquid.

**Residual Nitrogen usually returned as "Meat Bases."**—The sum of the percentages of nitrogen existing in the form of coagulable proteins, and albumoses and peptones (and of course gelatin when present) is subtracted from the total nitrogen; the residual nitrogen multiplied by 6.25 is usually returned as "meat bases." It is clear that when creatine and creatinine are estimated, the nitrogen present in these substances may be deducted from the total nitrogen, in which case the expression "meat bases" must be qualified by the additional words "other than creatine and creatinine." Perhaps, however, the best mode of expression is to state the percentage of "meat bases" as above, and to point out in an independent statement that this contains such and such a percentage of combined creatine and creatinine expressed as creatinine. It is suggested that no useful purpose is to be served by making separate estimations of these two bases. It will be interesting to have the views of the members on the employment of the arbitrary factor 6.25 for the conversion of residual nitrogen into the equivalent of so-called

"meat bases," and also on the question of the food value of the various groups of constituents mentioned in the above classification.

In order to make the discussion as practical as possible, it is particularly requested that proposals in reference to new or alternative processes of analysis should not be introduced except on the basis of experimental data.

Members desirous of taking part in the discussion are requested to communicate as soon as possible with the Hon. Secretary, R. H. A. PLIMMER, University College, Gower Street, London, W.C.

## CORRESPONDENCE.

### BRITISH LABORATORY WARE.

To the Editor of the Chemical News.

SIR,—We notice that in last week's CHEMICAL NEWS (cxii, 165) you have an account of the Exhibition held recently under the auspices of the University of Sheffield Scientific Advisory Committee.

Unfortunately your report mixes our exhibit with that of the British Laboratory Ware Association, Ltd., probably because we are members of the latter.

Our exhibit consisted of lamp blown ware, together with funnels, hydrometers, and thermometers, whilst that of the British Laboratory Ware Association, Ltd., consisted of beakers, flasks, glass tubing and test-tubes, porcelain ware, filter-papers, and nickel goods. And these two exhibits were distinctly separate ones.

We shall be glad if you will correct your report, as we have no desire to take that credit which should belong to the British Laboratory Ware Association, Ltd.—I am, &c.,  
J. PRESTON.

21, Holly Lane, Sheffield.

## MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Royal Institution, 3 "The War on Rheims," by Banister Fletcher, F.R.I.B.A.

THURSDAY, 22nd.—Royal Institution, 3. "The System of the Stars," by Prof. A. S. Eddington, F.R.S.

Royal Society. "Deep water Waves, Progressive or Stationary, to the Third Order of Approximation," by Lord Rayleigh. "A Chemically Active Modification of Nitrogen produced by the Electric Discharge" (VI.), by Hon. R. J. Strutt. "The Difference between the Magnetic Diurnal Variations on Ordinary and Quiet Days at Kew Observatory," by C. Chree. "Effects of different gases on the Electron Emission from Glowing Solids," by F. Horton. "Heats of Dilution of Concentrated Solutions," by W. S. Tucker. "Origin of the '4686' Series," by T. R. Merton. Chemical, 8.30. "Constitution of Internal Diazo-oxides (Diazo-phenols)," by G. T. Morgan and J. W. Porter. "Method for Distinguishing Tautomeric from Polymorphic Substances," by N. V. Sidgwick. "Metallo-compounds in Solution," by S. U. Pickering. "Studies on the Walden Inversion—Part I., The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid," by G. Senter and H. D. K. Drew. "Energy Distribution in the Radiation from the Ultraviolet Lamp," by A. J. Allmand. "Electromotive Forces in Alcohol—Part VI., Absolute Potentials by the Capillary Electrometer," by E. Newbery. "Absorption Spectra of the Vapours and Solutions of Anisol, Phenetol, and various Derivatives" and "Absorption Spectra of the Isomerides of Ammonium *d*- $\alpha$ -Bromo-camphor- $\beta$ -sulphonate," by J. E. Purvis. "Racemisation of Phenyl- $\beta$ -tolylactic Acid," by A. McKenzie and S. T. Widdows.

FRIDAY, 23rd.—Royal Institution, 9. "Military Hygiene at the War," by Major Percy S. Lelean, R.A.M.C.

Physical, 5. "Theories of Voigt and Everett regarding the Origin of Combination Tones," by W. B. Morton and Miss Mary Darragh. "Experiments on Condensation Nuclei produced in Gases by Ultra-violet Light," by Miss Maud Saltmarsh. "Self-induction of Solenoids of appreciable Winding Depth," by S. Butterworth.

SATURDAY, 24th.—Royal Institution, 3. "Modern Artillery," by Lieut.-Col. A. G. Hadcock, late R.A.

# THE CHEMICAL NEWS,

VOL. CXI., No. 2891.

## THYMOL: ITS MELTING- AND SOLIDIFYING POINT.

By ROBERT MELDRUM.

THERE is considerable variation in the published melting-points of thymol, as will be seen from the following figures:—44° C., Allen, Sprecker, Fownes, Cooley; 49.5° C., Bayley, 50° C., Roscoe and Schorlemmer, Thorpe, Kraugh. It would thus appear that two modifications of thymol exist, with melting-points of 44° and 50° C., or else that it undergoes a change on prolonged heating, which reduces its melting-point. The author has therefore undertaken the examination of the solidifying and melting of thymol under varied conditions, with the view of ascertaining the conditions which control variation from the normal. Unless otherwise stated, the same test tubes, 6 x 1 in., were used throughout the solidification tests, and the same thermometer, a 52° C. divided into tenths.

### The Solidifying-point.

*Method A.—Constant stirring in Air at 60° F.*—Melted thymol at various temperatures from 80° to 60° C. till all traces melted for varying periods and stirred with thermometer till temperature ceases to fall, and continued stirring till temperature rises to maximum; fixed thermometer in centre, 1 cm. from bottom of tube, and noted readings:—

Solidifying-point + rise, °C	48.5	48.5	48.5	48.5	48.5	48.5
Rise .. .. .	3.2	3.7	3.2	1.7	2.7	2.8

Minutes to fall from 52° C. to zero .. .. .	about 4
Minutes to rise from zero to maximum .. .. .	about 1
Minutes stationary at solidifying-point .. .. .	about 5

What takes place here is that, when lowest temperature is reached, on cooling fine crystals form in the melt, and as stirring is continued and temperature rises a shower of crystals fall to bottom of tube, the tube at same time becoming coated on one side to a depth of 2 mm. with crystals. When solidification is complete and temperature has fallen 1.5° C. below solidifying-point, about 70 per cent of contents of tube is still liquid; even when temperature has fallen 5° C. below maximum rise the greater part is still liquid. The remarkable feature of these experiments is the constant solidifying-point obtained and failure to attain solidification without supercooling. That complete solidification of contents of tube does not continue at 48.5° C., though ideal conditions are present, requires explanation. As solidification will not begin till supercooled, it is apparent the rising temperature stops crystallisation, and supercooling again requires to take place to again start crystallisation. Thymol, therefore, behaves on solidifying as if it were two different substances, one which solidifies at 48.5° C. and the other at a much lower temperature. But there can be no doubt the phenomenon is due to supercooling effect.

*Method B.—Stirred while being Cooled in Cold Water.*—Melted at 70° C. and cooled by stirring in air to 52° C., plunged tube into cold water at 8° C. and continued stirring till temperature ceased to fall and rose to maximum, and fixed thermometer 1 cm. from bottom of tube and in centre:—

Solidifying-point + rise, °C .. .. .	48.3	48.3	48.3
Rise, °C. .. .. .	11.3	9.7	11.8

Time to fall from 52° C. to zero and rise to maximum .. .. .	1½ mins.
Time thermometer stationary at maximum .. .. .	2 mins.

It is evident this method also yields constant results, though solidification is 75 per cent more rapid than when cooled in air by Method A. Failure to obtain normal solidifying-point is most likely due to temporary thermometer bulb and stem effects due to rapid cooling. The main point of these experiments is that supercooling is four times as great as by Method A, though cooled three times quicker, which points to the time factor as being essential for crystal formation. We here see the speed of crystallisation is slower than the rate of cooling. The whole contents of tube do not solidify at 48.3° C., but only part of same, complete solidification taking place as the temperature is lowered. After completion of above tests the thermometer was tested against a standard one and found correct.

*Method C.—Solidification while Partially Melted.*—Melted partially at 49° to 50° C. till about three-quarters melted, and stirred up crystals with the liquid. Removed from bath and stirred with thermometer till temperature ceased to fall, and fixed thermometer for readings:—

Solidifying-point + rise, °C	48.5	48.6	48.5	48.3	48.4
Rise, °C. .. .. .	0.0	0.6	0.1	0.2	0.0

As soon as thermometer is fixed all the crystals fall to bottom and attach themselves to sides. When thermometer has reached maximum and fallen to 48° C. one-half of thymol is still fluid. Though crystallisation has taken place under extra good conditions, and a fairly constant solidifying-point registered with minimum supercooling effect, yet the bulk of the thymol remains fluid. The time factor is here prominently brought out. The amount crystallised here per unit of time must be very small, as supercooling rapidly ensues. The solidifying-point by this method varies by 0.3° C., which is apparently due to small percentage crystallised, while the thermometer remains at maximum. Constant points cannot be expected when supercooling ensues so rapidly. It would appear that as the supercooling effect becomes eliminated the amount crystallised per unit of time decreases, resulting in a short period stationary-point, supercooling again commencing.

*Method D.—Cooled by Stirring in Hot Water Jacket.*—Melted thymol at 70° C. and cooled by stirring in air to 52° C., and placed tube in large hot water jacket at same temperature; stirred thymol and hot water jacket constantly, and allowed to cool at rate of cooling of water jacket:—

Solidifying point, + rise, °C	48.9	49.0	49.0	48.8
Rise, °C. .. .. .	0.4	0.2	1.5	0.8

During solidification tube is full of floating crystals, which rapidly fall to bottom on ceasing to stir. The shower of crystals fall from surface of thymol where supercooling must be present, due to contact of thymol with the air at 60° F. The rate of crystallisation is very slow, even with stirring, and apparently is slower than rate of cooling of large water jacket. This again points to the slow crystallising speed. What takes place here is solidification in surface layers, which are broken up by the stirring and dispersed through the mass. We have every reason to believe these layers are supercooled. The author has already pointed out this fact as regards mutton tallow (CHEMICAL NEWS, cxl., p. 37). From this it will be seen that large surface and small volume, and *vice versa*, will more or less modify solidification. A noted feature of above results is high solidifying points, which will require further explanation.

**Method E.—Cooling in Cold Water without Stirring.**—Melted at 70° C., and cooled by stirring in air to 52° C. Fixed thermometer in centre of tube 1 cm. from bottom and plunged into cold water at 8° C.:—

Solidifying-point + rise, °C.	44.8	46.0	43.5	44.7	39.7
Rise, °C. . . . .	19.2	26.8	24.8	24.5	16.5
Below normal, °C. . . . .	3.7	2.5	5.0	3.8	8.8
Minutes to cool from 52° C. to zero	..	..	..	..	5
„ „ rise .. .. .	..	..	..	..	5

The crystallisation sometimes takes place from surface of thymol and at other times from bottom of tube, and proceeds more or less in either direction, and sometimes in one direction only; at other times crystals start from sides of tube, and so on. The erratic zeros are due to bulb of thermometer being near or away from zones of crystallisation. Several times it was observed that while all the tube had crystallised the zone around bulb was fluid. Erratic solidifying-point is therefore due to location of zones of crystallisation in relation to thermometer bulb. Failure to attain normal solidifying-point is due to rate of supercooling being greater than rate of crystallisation. The experiments point to the great importance of stirring in breaking up the crystallising zones and producing a uniform dispersion of the crystals throughout the melt. Failure to attain the normal in numerous solidifying-point determinations of the fats and waxes is no doubt due to this cause.

**Method F.—Air Cooled without Stirring.**—Melted at 70° C. and cooled by stirring in air to 52° C., fixed thermometer 1 cm. from bottom of tube and in centre, and placed in apparatus to cool.

	A.	B.	C.	D.	E.
Solidifying-point + rise, °C.	43.6	41.8	45.4	41.7	44.7
Rise, °C. . . . .	7.6	4.0	18.0	9.2	15.5
Below normal, °C. . . . .	4.9	6.7	3.1	6.8	3.8
Minutes to fall 52° to zero	24	20	29	17	23
Minutes to rise .. .. .	30	20	60	20	19
Minutes stationary .. .. .	1.5	1	1	1	3

The nature of crystallisation here is exactly similar as under E. The same remarks apply. It is evident that heating and cooling is taking place at different speeds at different points in the tube. The rate of cooling here is from three to five times as slow as under E, and speed of crystallisation as measured by speed of rise is from five to twelve times as slow. These experiments show clearly how easily false solidifying-points may arise, not only as regards thymol but with other compounds. The following notes as to the nature of the crystallisation are of interest, and explain how false and erratic solidifications arise:—

A. Thermometer begins to rise while bulb is in liquid zone, and 1 cm. crystals at top and bottom of tube. At 43° C. crystallisation has extended upwards and downwards, just touching top and bottom of bulb. At maximum rise still partially liquid around bulb.

B. At 37.8° C. crystallisation has ascended from bottom of tube to bottom of bulb. All around bulb is liquid. At 41.8° C. nearly all liquid about bulb, and even after temperature has fallen 1°.

C. At 32° C. no crystals formed at bottom of tube. Bulb in fluid zone. At 27.5° C. 2 cm. crystals at top of thymol, but none at bottom.

D. At 32.5° C. crystals appear at bottom and top, and also a group on side of tube just above level of bulb. At maximum rise upper half of thymol still fluid.

E. At 29.2° C. crystals at both top and bottom of tube, and on side of tube above bulb level. At maximum rise partially fluid in centre of tube and around one side.

#### Speed of Crystallisation at various Supercooled Temperatures.

The author has measured approximately the speed of crystallisation at various supercooled temperatures by measuring the volume of crystals formed by means of a

graduated tube. Melted at 70° C. and cooled to 52° C. by stirring in air, fixed thermometer in tube, and allowed to supercool to indicated temperature, then rapidly stirred till thermometer rose to maximum and fixed thermometer for readings. Then removed thermometer and measured volume of crystals at bottom.

Supercooled to °C. . . . .	43.5	38.5	33.5
Solidifying-point + rise, °C. . . . .	48.4	48.4	48.2
Rise, °C. . . . .	4.9	9.9	14.7
Crystallised (per cent) .. .. .	25	50	65

As to be expected, the per cent of solidification follows the supercooling. The feature of these experiments is the large amount rapidly solidified when supercooled 15°, though a low solidifying-point is indicated. Moreover, though rapid and extensive crystallisation has taken place, yet the solidifying-points are from 0.8° C. to 0.4° C. lower than by Method D, where the crystallising rate is very slow. It would appear therefore that some conditions are present which lower the solidifying-point and which are not known, as the solidifying-point when determined by good methods shows a variation of 0.8° C. Even stearic acid, as the author has shown (CHEMICAL NEWS, cviii., 199), shows a difference also of 1° C. in its solidifying-point when the method of cooling is altered.

#### Solidification in Capillary Tubes.

In tubes and flat dishes of various diameters, the cooling being allowed to take place very slowly, thymol always solidifies within two hours. The author could not succeed in retarding solidification beyond that time. In capillary tubes of 1 mm. bore it may be maintained in the fluid condition for weeks with temperature of air at 50° F. The column of fluid thymol may be repeatedly moved up and down, and allowed to flow from one end of tube to the other, a distance of 6 cm., without solidification taking place. On touching end of tube with a little thymol powder solidification immediately takes place. On gradually cooling at the melting-point on large thermometer bulb to 15° C. liquid thymol may be obtained in large drops at apex of bulb, which may be moved up and down bulb by tilting without solidification taking place.

A most interesting experiment as regards the solidification of thymol is by melting thymol at 60° to 70° C. in tube, and immersing thermometer in same till it attains same temperature, withdrawing, and exposing to air at 2° C. When thermometer has fallen to this temperature a large drop of thymol is on apex of bulb, which may be worked up and down and about bulb without solidification taking place. When solidification does take place it starts about 5 cm. up stem and slowly increases downwards towards apex, which may take fifteen to twenty minutes. From this and the behaviour of thymol in capillary tubes it would appear that surface tension is the cause of failure to solidify.

#### Melting-point of Thymol.

##### Thermometer Bulb Method—

48.7	49.0	49.0	49.3	49.2 °C.
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These are the temperatures at which first drop appears. The drops are very slow in forming.

**Opacity Method.**—Ten grms. in test-tube,  $\frac{3}{4}$  x 6 ins., and heated in water-jacket at the rate of ten minutes per degree. Stirred jacket all the time, and also thymol as soon as sufficiently fluid. Heated till all traces melted.

50.1	50.1	50.0 °C.
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**Floating on Water Method.**—Placed 1 grm. in 200 cc. water, and heated very gradually. Stirred water slowly. Melts at 43° C., and solidifies at 42° C. It is clear that water lowers the melting-point, no doubt due to hydration.

*Influence of Water on the Solidifying-point.*

Twenty grms. thymol in tube 1 1/32 inch bore to which was added, roughly, 0.25 cc. water. Heated to 70° C., and stirred; the greater part of the water does not dissolve, but falls to bottom as a globule.

*Solidifying-point by Method A.*

Solidifying-point + rise, °C...	45.4	45.3	45.6
Rise, °C. . . . .	4.4	2.3	3.6

Supercooled to 43° C. and stirred. Temperature fell to 40° C.

Solidifying-point + rise, °C. . .	45.5
Rise, °C. . . . .	5.5

Added about 1 cc. more of water = to about 6 per cent. Nearly all water at bottom; will not dissolve.

Solidifying-point + rise, °C. . .	40	39.9
Rise, °C. . . . .	8	1.4

*Thymol with 1 per cent Water.*

Ten grms. of thymol with 0.1 cc. distilled water in test-tube, 6 x 1/2 in. The thymol previous to adding water gave a solidifying-point of 49.2° C. with three determinations. After adding water the results were:—

48.15 47.50 47.1 46.0 45.7 45.1 45.1 °C.

Each time the thymol is solidified and re-melted more water goes into solution or combination. At 45.1 all water has disappeared. This shows that 1 per cent water lowers the solidifying-point by 4.1° C. It was found 2 per cent lowers it 6.2° C.

These facts explain to a considerable extent the variation in the solidifying-point of thymol due to moisture in the air, tubes, and the thymol itself. The tests indicate that a little more than traces of moisture may lower the solidifying-point by nearly 1° C. Though solid thymol does not absorb moisture in the same manner as phenol, yet in the melted condition it behaves in a similar manner.

*Influence of Bore of Tube on Solidifying-point.*

The author has previously investigated the influence of bore of tube in the solidification of spermaceti (CHEMICAL NEWS, cxi., 37), with negative results. That the bore of tube affects the solidifying-point of thymol will be seen from following results:—

*Tube 1-1/2 in. Bore by Method A.*

Solidifying-point + rise, °C. . .	48.65	48.65	48.65
Rise, °C. . . . .	6.6	4.6	5.1

*Supercooling in Air and Stirring Method.*

Supercooled to °C. . . . .	47	45	43
Falls on stirring to °C. . . .	45.5	44	41
Solidifying-point + rise, °C. .	48.7	48.7	48.7
Rise . . . . .	3.2	4.7	7.7

*Tubes 22/32 and 16/32 in. Bore by Method A.*

Solidifying-point + rise, C. . .	49.2	49.2	49.2
Rise, °C. . . . .	2.2	2.5	3.0

Here the solidifying-point is lowered 0.55° C. by increasing diameter of tube. This may be due to larger surface of melted thymol being exposed to moisture in air. But the theory which agrees with actual facts is that it is due to ratio of surface of tube to volume. As diameter of tube increases, surface area decreases and volume increases. The final result being that more matter is crystallised per unit of time in proportion to volume with narrower tubes. This would apply to all substances having the supercooling effect.

*Thymol and Oil of Thyme.*

Twenty per cent oil thyme + 80 per cent thymol in tube 6 x 1/2 in. Solidifying-point by Method A.

Solidifying-point + rise, °C	38.8	38.8	38.6	38.8	38.7
Rise, °C. . . . .	0.8	1.3	3.6	3.8	0.7

About one-third only solidifies at 38.8, even on allowing to cool to 36° C. After maximum rise, crystallisation slows down or almost ceases. If stirring is continued too long when solidification begins a setting point of only 37.5° will be reached.

*Effects of Supercooling of Mixture.*

Supercooled to °C. . .	38	36	34	32	30	28	26
On stirring falls to °C. .	35	35	33	30	28	26.5	25
Solidifying - point + rise, °C. . . . .	38.6	38.1	37.7	37.2	36.6	36.3	35.6
Rise, °C. . . . .	3.6	3.1	4.7	7.2	8.6	10.2	10.6
Below normal, °C. . .	0.0	0.7	1.1	1.6	2.2	2.5	3.2

When the mixture of thymol and oil is allowed to cool to 15° C. for twenty-four hours the oil separates out indicating that the oil is not soluble in thymol at that temperature. Apart from any question of solubility it does not form a homogeneous solid, like mixtures of the solid and liquid fats, but yields a solidification more like a deposit of salt from a saline solution. Failure to reach the normal solidifying-point when supercooled is no doubt due, like thymol itself, to speed of crystallisation. The indicated solidifying-point lowers with supercooling. This is the explanation of many false solidifying-points of mixtures of solids and liquids. Solidification in hot water-jacket = 39° C.

*Melting point of Mixture.*

By the opacity method; heating slowly in test-tube in hot-water jacket till all traces melted. Three determinations gave 41° C. The melting-point is therefore 2.2° C. higher than setting point.

*Summary.*

The solidifying point of thymol varies between 48.2 and 49.2° C. The variation is due to bore of test-tube and absorption of moisture by thymol. The higher figure is to be accepted, as it approaches more closely the melting-point.

## DETERMINATION OF COPPER IN STEEL.\*

By W. D. BROWN.

In view of the increased use of copper in steel as a preventive of corrosion and of the necessity of completing the determination in a very short time, a rapid and accurate method for the determination of copper in steel is essential to a steel works laboratory.

The precipitation of copper by potassium or ammonium thiocyanate solution has been used in the gravimetric determination of copper. Van Name has shown that, under certain conditions of concentration, acidity, &c., the precipitation is complete (*Am. Journ. Sci.*, x., 451; xii., 20; and Gnoch's "Chemical Analysis," p. 108). Treadwell and Hall describe a method for the titration of cuprous thiocyanate, CuCNS, with potassium iodate ("Analytical Chemistry," 1914, ii., 672; 1910, p. 599; see also *Journ. Am. Chem. Soc.*, 1908, xxx., 760); in this titration iodine is at first set free and absorbed by the chloroform added as an indicator, then oxidised by more iodate to iodine chloride, the violet colour disappearing from the chloroform.

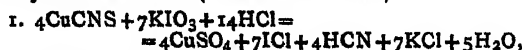
In the method submitted here potassium iodate is used

\* Presented before the Pittsburg Section of the American Chemical Society, January 21, 1915. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 7.

in excess, and the excess, after the addition of potassium iodide, is titrated with sodium thiosulphate.

**Method.**—Five grms. of steel are dissolved in 65 cc. of a mixture of 40 cc. nitric acid (1.20 sp. gr.), and 25 cc. sulphuric acid (1.1), and the solution evaporated to fumes of sulphur trioxide in a covered porcelain dish over a high flame; care must be taken that all nitric acid is expelled. The dish is removed from the heat, and, when cold, 50 cc. of hot water are added, and the solution boiled, transferred to a No. 5 beaker, and diluted to 400 cc. with hot water. When all the ferric sulphate is in solution, 50 cc. strong ammonium bisulphite are added while stirring, followed by 25 cc. of 5 per cent potassium thiocyanate. The solution is boiled until precipitation is complete, which requires five minutes, and filtered by suction through a 11 cm. No. 0 Munktell filter, the precipitate and beaker being washed with cold 1 per cent sulphuric acid solution. Paper and precipitates are transferred to a beaker, 20 cc. hydrochloric acid (1.1) are added, followed by standard potassium iodate solution (2 cc. for each 0.1 per cent copper expected). The paper is well macerated with a glass rod, and water added to a volume of 500 cc.; the potassium iodide solution is now added (1 cc. of 10 per cent solution for each cc. of iodate added), and free iodine titrated with standard thiosulphate solution; the thiosulphate should be added rather slowly, and the solution stirred vigorously, care being taken that no part of the solution is bleached before the whole. When the yellow colour of free iodine has nearly vanished, 5 cc. starch solution are added, and the titration continued until the blue is bleached. The difference between the iodate and thiosulphate represents the copper.

**Calculations.**—The reactions and calculations are rather intricate. The iodate when in excess oxidises the copper thiocyanate as follows (Treadwell and Hall):—



from which it is seen that  $7\text{KIO}_3$  oxidise 4Cu and an iodate solution made accordingly gave correct results on titration using chloroform. If now the solution be diluted and an excess of potassium iodide be added the iodine chloride, ICl, will be changed to free iodine according to the reaction—

2.  $7\text{ICl} + 7\text{KI} = 14\text{I} + 7\text{KCl}$ ;  $7\text{KIO}_3$  oxidise 4Cu and at the same time liberate 14I, or  $1\text{KIO}_3$  liberates 2I. The excess of  $\text{KIO}_3$  has been reduced by potassium iodide according to the reaction—

3.  $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + 6\text{I}$ , from which it follows that one  $\text{KIO}_3$  in excess liberates 6I, whereas each  $\text{KIO}_3$  which oxidises copper liberates 2I or one-third the former.

Therefore one-third of the oxidising power of potassium iodate is reclaimed on addition of potassium iodide. It was shown that  $4\text{Cu} = 7\text{KIO}_3$  in concentrated acid solution (1). In dilute solution, after addition of potassium iodide,  $4\text{Cu} = \text{two-thirds of } 7\text{KIO}_3$  or  $1\text{Cu} = \frac{7}{6}\text{KIO}_3$ .

For the above titration 1 cc. should equal 0.1 per cent copper on a 5 gm. sample, or 1 cc. = 0.005 gm. copper. Then 1 cc. should contain  $0.005 \times 7\text{KIO}_3/6\text{Cu}$ , or 1000 cc. should contain 19.64 grms. potassium iodate. A solution of potassium iodate was standardised with sodium thiosulphate against potassium permanganate which had been standardised against sodium oxalate, and it was found that the "C.P." salt contained but 97 per cent of its theoretical oxidising power, there being some potassium carbonate present as well as other impurities. Taking this into consideration the solution of potassium iodate is made by dissolving 20.2 grms. salt and diluting to 1 litre. The solution of sodium thiosulphate is made by dissolving 137 grms. per litre, and is made to agree with the iodate solution if necessary. These solutions are best standardised against permanganate in the well-known way.

**Results.**—On determining copper on a solution of copper sulphate containing the equivalent of 0.25 per cent copper, good results were obtained.

### Results on a Copper steel Standard

Laboratory.	Method	Per cent Cu
1.	Not given .. .. .	0.216
2.	Not given .. .. .	0.21
3.	Not given .. .. .	0.21
4.	Not given .. .. .	0.224
	Electrolysis .. .. .	0.224
5.	Vol. and elec. .. .. .	0.205
6.	Electrolysis .. .. .	0.21
7.	Electrolysis .. .. .	0.204
8.	Not given .. .. .	0.21
9.	Not given .. .. .	0.206
	Not given .. .. .	0.214
10.	Not given .. .. .	0.21
	Duquesne grav. $\text{CuO}$ .. .. .	0.215
	Duquesne vol. $\text{KIO}_3$ , $\text{Na}_2\text{C}_2\text{O}_4$ std. .. .. .	0.213
Average .. .. .		0.212

Results by steel works laboratories on a copper steel standard as given above.

## ELECTROLYTIC REFINING OF GOLD.\*

By Sir THOMAS KIRKE ROSE.

(Concluded from p. 184).

### Gold Chloride Process.

THE solution used in the bath contains gold in the form of chloride and some free hydrochloric acid. Gold is dissolved at the anode, under the action of a current of electricity, and deposited in a pure state at the cathode. Other metals are also converted into chlorides at the anode, and either enter into and remain in solution or pass into the anode slime.

Gold is dissolved at the anode both in the aurous and auric condition with the formation of hydrogen aurichloride,  $\text{HAuCl}_4$ , and hydrogen aurochloride,  $\text{HAuCl}_2$ . The ions of these are respectively  $\text{H}_2\text{Au}^+$  and  $\text{AuCl}_4^-$ ;  $\text{H}_2\text{Au}^+$  and  $\text{AuCl}_2^-$ . According to Wohlwill there is evidence that the gold chlorides  $\text{AuCl}_3$  and  $\text{AuCl}$  are not formed, and that gold does not go into solution under the action of the current unless the conditions are such as to favour the production of the ions  $\text{AuCl}_4^-$  or  $\text{AuCl}_2^-$ . It is at least certain that if the bath contains only  $\text{AuCl}_3$  or  $\text{HAuCl}_4$ , without free hydrochloric acid, chlorine is evolved at the anode and scarcely any gold is dissolved, although precipitation proceeds normally with impoverishment of the bath.

Impoverishment of the bath is also caused by the presence of impurities in the anodes even if no chlorine is evolved. Part of the current is employed in dissolving the impurities, and as gold alone is deposited at the cathodes the amount in solution is reduced, and it is necessary to add chloride of gold at stated intervals. Wohlwill observes that with bullion containing, for example, gold 83, silver 15, copper 2 per cent, about 14.5 per cent of the alloy must be dissolved chemically (*Electro-Chem. and Met. Ind.*, 1904, ii., 261). In making this calculation allowance is made for the fact that there is a tendency for the electro-chemical equivalent of gold to be higher at the anode than at the cathode, especially in hot solutions, or, in other words, a tendency towards the enrichment of the bath. Impoverishment of the bath leads to a soft dark coloured gold deposit, which is not firmly adherent to the cathode and is difficult to wash.

When silver is contained in the anode it is converted into silver chloride, which in part dissolves, in part falls to the bottom of the cell, and in part adheres to the anode, forming an insoluble coating. The result of the coating is that the resistance to the passage of the current in-

\* Presidential Address, delivered before the Institution of Mining and Metallurgy, March 18, 1915.



creases, the free area of the anode is reduced, the density of the current becomes greater per unit area of effective anode surface, and chlorine is evolved unless a very small current is used. According to general experience, if more than 6 per cent of silver is present in the bullion of the anode the ordinary remedies (addition of more hydrochloric acid or heating the solution) are no longer sufficient, and it is necessary to brush the silver chloride from the anodes.

An alternative method now adopted in the most modern refineries is the use of a pulsating current in the place of the simple direct one. This is obtained by superposing on the latter an alternating current of greater maximum voltage than the direct current (German patent 207,555, Sept. 22, 1908; English patent 6276, 1909; *Met. and Chem. Eng.*, Feb., 1910, p. 82; Report of the Director of the U.S. Mint, 1912, p. 49; 1913, p. 41). The result is that the direct current is alternately reinforced and reversed. At the Denver Mint, for example, the E.M.F. of the direct current is 1.2 volts, and that of the alternating current a maximum of 1.8 volts.

Under the action of the pulsating current the silver chloride formed by the direct current is stripped off and falls to the bottom of the tank. This is probably a mere mechanical effect due to the evolution of a small quantity of gas at the anode, said by the patentees to be oxygen. The proportion of silver in the anodes may by this device be increased to at least 17 per cent without scraping, and much rough gold can be passed at once to the gold cells without previous treatment in the silver nitrate solution.

In the first month after the introduction of the pulsating current in the Denver Mint, in April, 1913 (Report of the Director of the U.S. Mint, 1913, p. 42), the number of silver cells was diminished by one-half, and the cost of operating the refinery was reduced from 3.2 cents per ounce of fine gold to 2.0 cents per ounce. Against this cost is to be set 0.34 cent per ounce, the value of the by-products. The anode melt of the lowest gold fineness contained gold 80.47, silver 17.16, and the cathode was 99.5 fine in gold.

The quantitative electrolytic effect is unaffected by the alternating current. In other words, the total gold deposited on the cathode can be found from Faraday's law, on the supposition that only the direct current is passing.

The application of Faraday's law is, however, subject to an important qualification. The electro-chemical equivalent of trivalent gold corresponds to a deposition of 2.45 grms. per ampère hour, and that of monovalent gold to one of 7.35 grms. per ampère hour. In ordinary work a mixture of the two is deposited, and the total is often about 2.5 grms. per ampère hour, but it varies in every bath with the composition of the electrolyte, with the temperature, and with the current density. Wohlwill observes that "so little evidence was found of that constancy of weight of deposit under the most varied conditions that would be expected according to Faraday's law that it would be scarcely too much to say that, if Faraday had restricted his researches to solutions of this kind, he would never have arrived at a knowledge of his law."

According to Wohlwill, with what he calls high current densities, e.g., 800 to 1000 ampères per sq. m., the amounts dissolved and deposited approach one another and approximate to the 2.45 grms. per ampère hour, corresponding to trivalent gold, and under these conditions the amount of gold deposited in the anode sludge, owing to the decomposition of  $\text{HAuCl}_2$  in contact with water, reaches a minimum.

According to my own experiments the temperature of the bath has far more effect in these respects than the current density up to 1000 ampères per sq. m.; at higher densities, as will be shown later, the results are different. A hot bath causes a considerable amount of monochloride of gold to be formed in the bath at moderate current densities, and the quantity of gold or other metals dissolved at the anode is greatly in excess of that deposited at the cathode. As an example, the following typical re-

sults are appended, obtained with anodes containing only a small proportion of silver, with a bath containing 5 per cent of gold and 5 per cent of free HCl.

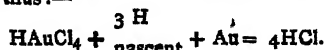
TABLE II.

	Current per sq metre Ampères.	Temp.	Anode loss per ampère hour Grms	Gold deposited at cathode per ampère hour. Grms
1.	400	17°	2.65	2.54
2.	1000	17°	2.54	2.44
3.	1000	67°	4.26	3.19

The excess of gold dissolved at the anode is in great part reprecipitated at once by decomposition of the monochloride, although the latter is much more stable in hot hydrochloric acid than in cold water. In hot solutions the amount of gold accumulating in the anode slime at a current density of 1000 ampères per sq. m. is thus far greater than that in cold solutions. This is a point in favour of cold solutions which may account for their increasing use in place of the hot solutions employed at first.

To give an instance from practice. At the Denver Mint, where a hot bath is used, the temperature being 65°, the amount of gold found in the slime was 11.37 per cent of the fine gold deposited on the cathodes, with the pulsating current, the direct current density being 65 ampères per sq. ft., or 700 ampères per sq. m. of cathode (Report of the Director of the U.S. Mint, 1913, p. 42). Previously, when the direct current alone was used, the slime contained an amount equal to 17.19 per cent of the gold deposited on the cathodes. The amount of gold in the slime in practice with cold baths is lower, but is not published. In my own work I find it to be less than 1 per cent, exclusive of the butt ends of anodes.

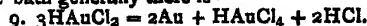
The electrolysis of  $\text{HAuCl}_4$  results in the migration of H ions towards the cathode and of  $\text{AuCl}_4$  ions towards the anode. Hydrogen is set free at the cathode and in its nascent state replaces gold in solutions containing  $\text{HAuCl}_4$  and  $\text{HAuCl}_2$ , precipitating the gold and producing hydrochloric acid. The cathode reactions may be represented thus:—



At the anode,  $\text{AuCl}_4$  being set free splits up into  $\text{AuCl}_3$  (which has some effect in dissolving gold in hot solutions) and chlorine, which is either evolved or used in dissolving the gold. Similarly,  $\text{AuCl}_2$  set free at the anode splits up into  $\text{AuCl}$  and chlorine. The  $\text{AuCl}$  either combines with HCl to form  $\text{HAuCl}_2$  or decomposes into metallic gold, which is precipitated, and  $\text{AuCl}_3$ . The reactions at the anodes may be expressed as follows:—

1.  $\text{AuCl}_4 = \text{AuCl}_3 + \text{Cl} (\text{nascent}).$
2.  $\text{AuCl}_2 = \text{AuCl} + \text{Cl} (\text{nascent}).$
3.  $\text{AuCl}_3 + \text{HCl} = \text{HAuCl}_4.$
4.  $\text{AuCl} + \text{HCl} = \text{HAuCl}_2.$
5.  $\text{Au} + 3\text{Cl} (\text{nascent}) + \text{HCl} = \text{HAuCl}_4.$
6.  $\text{Au} + \text{Cl} (\text{nascent}) + \text{HCl} = \text{HAuCl}_2.$
7.  $\text{AuCl}_3 + 2\text{Au} + 3\text{HCl} = 3\text{HAuCl}_2.$
8.  $3\text{AuCl}_3 = \text{AuCl}_5 + 2\text{Au}.$

In the bath generally there is—



Equations Nos. 8 and 9 cause gold to pass into the anode slime.

The effect both of these chemical reactions and of the migration of the ions is to impoverish the solution in gold near the cathodes and to enrich it at the anodes, and it is accordingly necessary to stir the solution. The usual method is to use a glass or hard rubber propeller in the tank, making 200 or 300 revolutions per minute. This occupies some of the space in the tank, thus reducing

its capacity, and also it drives particles of silver chloride against the cathode, where they adhere, reducing the fineness of the gold and leading to the adoption of a second refining in other tanks at San Francisco (Durham, *Eng. and Min. Journ.*, Nov. 11, 1911, p. 951). To overcome the difficulty a cascade system of mixing was advocated by R. L. Whitehead (*Electro-Chem. and Met. Ind.*, Sept., 1908, p. 355). The method has the incidental advantage of keeping the solution of the same composition in all the cells, and it is about to be adopted in the New York Refinery, the solution being raised by a hard rubber pump (private communication, dated Jan., 1915, from Mr. B. P. Wirth, the Superintendent of the Melting and Refinery Dept., New York Assay Office).

A word as to impurities. It does not appear to be usual to remove the base metals from low-grade bullion by a preliminary toughening operation, but the objections to this course are not obvious. It would be especially desirable to prevent any large amounts of lead, bismuth, or tellurium from entering the electrolytic cells, as traces of these metals make gold brittle.

**Recovery of Platinum.**—As for the platinum metals, iridium and osmium are insoluble and remain with the anode slime. Platinum is insoluble if it is nearly pure, but if present in small quantities alloyed with gold and silver it passes into the solution and remains there. Palladium behaves similarly.

To prevent the cathode deposit from being contaminated with platinum it is necessary, according to Wohlwill, that the amount of platinum in the bath shall not be more than about 50 grms. per litre. This must refer to a hot bath, as I have found that in a cold bath containing only 20 grms. per litre some platinum is deposited with the gold. This is not the case with hot baths of similar strength, as is shown by the following results of electrolysis a solution containing 2 per cent of platinum and 5 per cent of gold:—

TABLE III.

Temp.	Ampères per sq. metre of cathode.	Platinum contained in deposited Gold.
1. 20°	400	0.6 per 1000
2. 20°	800	1.0 per 1000
3. 67°	400	Nil.
4. 67°	800	Nil.

R. Pearson (44th Annual Report of the Mint, 1913, p. 182) at the Ottawa Mint found a distinct trace of platinum in cathode gold in both hot and cold cells, but does not give the composition of the electrolyte. The current density which he used was apparently about 225 ampères per sq. m.

The objection to the use of cold baths in the treatment of platiniferous gold does not apply, however, in the treatment of ordinary bullion owing to the smallness of the proportion of platinum which is present. In the year ended June 30, 1913, for example, the United States Mints recovered the following amounts of platinum and palladium in treating over 3,000,000 ozs. of gold bullion (Report of the Director of the U.S. Mint, 1913, p. 22).

	Sponge platinum.	Sponge palladium.
San Francisco ..	205.74 oz.	—
Denver .. ..	58.20 oz.	10.15 oz.
New York .. .	1403.00 oz.	18.10 oz.
	1666.94 oz.	28.25 oz.

D. K. Tuttle reported in 1903 (Report of the Director of the U.S. Mint, 1903, p. 63) that there was no platinum in Klondike gold nor in bullion produced by American chlorination or cyanide mills. The platinum recovered in the United States Mints is derived, he says, only from dental and jewellers' scrap. E. L. Entwistle finds (private communication, 1914) that about 10 ozs. of platinum are recovered per 100,000 ozs. of the gold refined at Ottawa, which is received in about equal quantities from the Yukon and Porcupine.

The occurrence of platinum in gold from the Witwatersrand is now well known (C. B. Horwood, *Min. and Sci. Press*, Nov. 8, 1913, p. 724), but no details are available as to the exact proportion present. In any future consideration which may be given to the refining of Rand gold this point must be taken into account.

#### Current Density and Composition of Electrolyte.

There are considerable differences in the current densities employed. Wohlwill observes (Borchers and McMillan, *op. cit.*, p. 366) that in normal work a current density of as much as 1000 ampères per sq. m. of electrode could scarcely be usable. Nevertheless he states that with fine gold anodes a density of 3000 ampères per sq. m. of anode surface is possible, with 3 per cent. of hydrochloric acid in the bath, and he calculates that under these conditions gold anodes 4 mm. thick would be completely dissolved in five hours. This seems to be an exaggerated claim, but it is true even of less pure gold if the bath is stronger in acid, as is shown later. Silver in the anodes, as already stated, has been found to necessitate a lower current density. In practice in Germany a current density of 400 to 500 ampères per sq. m. is used. In America various current densities of from 700 to 1000 ampères per sq. m. (65 to 93 ampères per sq. ft.) are employed, and anodes of  $\frac{1}{8}$  in. thickness require from 40 to 60 hours to dissolve, or about a week, as night work is nowhere the rule.

A high current density is obviously desirable in order to expedite the work, and the density attainable depends on the composition of the electrolyte and that of the anodes.

The electrolyte is conveniently considered in two parts, the conditions at the anode depending on the amount of free hydrochloric acid present, and the deposition at the cathodes depending on the amount of gold chloride in solution. In a hot bath more rapid work can be done at both anode and cathode than in a cold bath.

**Dissolution of Gold at the Anodes.**—The amount of free hydrochloric acid recommended by Wohlwill is 3 per cent in a hot bath, and in America 5 or 6 per cent is now used in hot baths and 10 to 12 per cent in cold ones, but it would appear that still higher percentages offer certain advantages, as is shown in the following table, in which a summary of some experiments of my own is given:—

TABLE IV.

Composition of anode.	Temp.	Free HCl present. Per cent.	Current density per sq. m. below which no chlorine is evolved.	Ampères
1. Pure Gold ..	20° to 90°	Nil.	Less than	90
2. { Gold.. 930 Silver 50 Copper 20 }	20°	10	Less than	800
3. Do... ..	20°	12	Less than	900
4. Do... ..	67°	11	Less than	1000
5. Do... ..	20°	20	Over ..	3330 less than 5000
6. { Gold.. 985 Silver 10 Copper 5 }	25°	12	Less than	2065
7. Do... ..	45°	12	Less than	3100
8. Do... ..	25°	20	Over ..	3300
9. { Gold.. 780 Silver 195 Copper 25 }	40°	29	About ..	3000
10. Do... ..	62°	29	About ..	5000

In the table "less than x ampères" means that the evolution of chlorine was just perceptible at that current density, but it is obvious that a little chlorine would not prevent the work from being done. In experiments Nos. 9 and 10 isolated bubbles of chlorine were formed and given off at the anode at particular points where for the moment silver chloride adhered firmly. With an anode containing 20 per cent of silver, in a bath at 62° containing 29 per cent of free hydrochloric acid, using a current of 5000

ampères per sq. m., the amount of chlorine evolved was small and did not perceptibly affect the progress of the work. The loss of efficiency of the current due to the evolution of chlorine was insignificant.

With heavy currents, *e.g.* over 3000 ampères per sq. m. (250 ampères per sq. ft.), the amount of silver in the anode is of comparatively little effect, as the silver chloride flakes off readily under the action of the current. I see no reason for limiting the silver to 20 per cent. All this refers to work with the direct current alone. I have made no experiments with the pulsating current.

A heavy current heats the solution, and in experiments Nos. 9 and 10 the temperatures of 40 and 62 deg. were not deliberately aimed at, but were the result of the passage of the currents named, and could not be kept lower, in spite of means being taken to cool the baths.

With currents of 3000 ampères or more a hot solution has no effect in increasing the amount of gold passing into the anode slime, thus:—

TABLE V.

Composition of anode.	Temp.	Acid.		Current density per sq. m. Amperes.	Percentage of gold passing into slime. Per cent.
		Per cent.			
1. Pure gold ..	20	5		750	0.8
2. Do. ..	67	5		750	30.1
3. { Gold.. 930 Silver 50 Copper 20 }	20°	12		900	0.2
4. Do. ..	67	12		1000	16.5
5. { Gold.. 985 Silver 10 Copper 5 }	17°	20		1000	1.0
6. Do. ..	45°	20		3300	0.1
7. { Gold.. 780 Silver 195 Copper 25 }	62°	29		5000	0.08

Table V. goes to prove that as the current density is raised the amount of gold passing into the slime, whether as detached fragments of anode or as reprecipitated gold, diminishes, and that this effect is more powerful than that due to temperature. Above 3000 ampères per sq. m., as in experiments Nos. 6 and 7, practically no gold passes into the slime, even in a hot bath. Even the minute quantity found there appears to consist entirely of detached fragments of anode.

In other experiments the anodes were enclosed in cotton bags to separate the gold precipitated by the decomposition of dissolved monochloride of gold from that consisting of detached fragments of anode or precipitated at the moment of dissolution. It was found that at 1000 ampères per sq. m. over 90 per cent of the slime-gold was retained in the bag, and that the slime-gold in the bag was of higher fineness than the anode gold, so that part of it consisted of metal which had been dissolved and reprecipitated as pure gold.

The general conclusion from these experiments is that with 20 to 30 per cent of free hydrochloric acid in the bath a current density of 3000 to 5000 ampères per sq. m. of anode surface can be maintained, and that the bath need not be heated externally. The percentage of silver, as far as the experiments went, appears to be of little importance at such densities. At 5000 ampères per sq. m. (464 ampères per sq. ft.) an anode of  $\frac{3}{8}$  in. thick would be dissolved in about seven hours. Anodes of such a thickness are not difficult to cast, but as an alternative they could be cast thicker and rolled down. The increase in the cost of acid caused by such conditions would be infinitesimal per ounce of gold. No experiments were made with the pulsating current, which seems to be less needed under such conditions.

**Deposition of Gold at Cathodes.**—It is recommended by Wohlwill that the proportion of gold present as chloride in the bath should be  $2\frac{1}{2}$  to 3 per cent, and strengths of 3 to 7 per cent are in use in America. The rate of deposi-

tion, however, may be increased if stronger solutions are used. It is generally considered desirable that the cathode deposit should be coherent, to enable it to be washed readily. At Ottawa, according to Entwistle (private communication, 1914) the deposit of gold on the cathode at 500 ampères per sq. m. of surface is a black slime in cold solutions containing 5 per cent of gold, but is a yellow-coloured coherent sheet at 50° at the same current density. In the United States Mints a current density of 1000 ampères in a cold solution with 7 per cent of gold appears to give a satisfactory deposit. A summary of the results of some experiments of my own is as follows:—

TABLE VI.

Gold in solution. Per cent.	Temp.	Current density per sq. m. of cathode.	Nature of deposit.
1. 3.0	20°	300	Dark, pulverulent.
2. 7.3	20°	200	Brown coherent sheet.
3. 8.1	20°	400	Brown coherent sheet.
4. 8.1	20°	440	Not perfectly coherent.
5. 7.7	20°	500	Brown, pulverulent.
6. 7.5	67°	500	Yellow, coherent.
7. 13.5	20°	1100	Brown, coherent.
8. 13.5	20°	2000	Brown, pulverulent.
9. 20.0	25°	1500	Yellow coherent sheet.
10. 20.0	40°	2000	Yellow coherent sheet.
11. 20.0	62°	5000	Brownish yellow continuous coating, adherent to cathode, but soft. Partly disintegrates when removed by scraping.

It is clear that coherent sheets of gold can be obtained with higher current densities when solutions stronger in gold are used, but that it does not seem likely that the high current densities indicated for the anodes can be used for cathodes if hard coherent sheets are to be obtained. In a cold bath, with 3 per cent of gold in solution, the limit of coherence is already passed at 300 ampères, and with 8 per cent of gold, the limit lies between 400 and 440 ampères. With 13.5 per cent the limit is above 1100, and with 20 per cent not less than 1500 ampères. In a hot bath considerably higher densities are attainable, as the table shows, and as experience in practice proves.

There is another possibility to be considered. The pulverulent precipitates do not consist of fine slime but of loosely agglomerated nodules in excellent condition for being washed in a suitable filter. No tendency has been observed for rapidly deposited gold, up to the limits of my experiments, to be of lower fineness than slowly deposited gold, after similar washing. The fineness of the cathode deposit in experiment No. 11, Table VI., was 997.7 in gold and 2.3 in silver. The anode contained 195 per 1000 of silver.

The presence of a little silver and copper in cathode gold does not reduce its quality or detract from its value. Dark coloured gold, washed and melted, is as fine and malleable as yellow gold similarly treated. The only difficulty is that in cold solutions the nodules of gold may fall to the bottom of the tank if rapidly deposited instead of adhering to the cathode. That difficulty could be met by enclosing the anodes in cotton bags and providing trays below the cathodes, but if hot solutions are used the difficulty does not arise. The provision of anode bags does not ensure that the cathodes will be pure gold. In an electrolyte containing 25 per cent of free hydrochloric acid and 20 per cent of gold the amount of silver in the form of chloride kept dissolved in the bath is 0.08 per cent. By heavy currents some silver appears to be electro-deposited from this solution with gold, making it less fine, as in experiment No. 11, Table VI.

If a heavy current is suddenly turned on, there is a vigorous evolution of hydrogen at the cathode. To avoid this, it is necessary to begin gradually, increasing the

current by degrees. After about 20 min. no hydrogen can be detected at 5000 amperes per sq. m.

Naturally the stronger the solution, the more care must be exercised to avoid loss through drips and splashes. There is also the loss of interest on the value of the solution to be considered. There should be no difficulty in arriving at the most economical point if the problem were fairly faced at one of the refineries.

There is a further point about the cathodes. In practice, they have always consisted of sheets of pure gold, which are melted with the deposit. The result is that at Ottawa, out of 4000 oz. of cathodes, 600 oz. are rolled out for the manufacture of new cathodes, and although at San Francisco the proportion is considerably less, the work of rolling large plates down to 0.01 or 0.02 in. thick is necessarily arduous. This can be avoided by covering the plates with a protective coating such as a mixture of graphite and beeswax, or for temperatures above 60°, graphite and Chinese wax. If this is done the most strongly coherent deposit is readily split off and there is no need to use gold for the permanent cathode.

I have found copper to be useless for cathodes, but silver plates answer very well and can be used of any desired thickness with a saving of interest on the value locked-up (silver cathodes have already been suggested by R. L. Whitehead, *Electro-Chem. and Met. Ind.*, Oct., 1908, p. 410, but have not been used). Most of the experiments mentioned in this address were made with protected silver cathodes. The evolution of hydrogen mentioned above is more perceptible with cathodes of silver than those of gold, but the efficiency of the current is still high at 5000 amperes, the deposit of gold being at the rate of 2.39 grm. per ampere hour, corresponding to an efficiency of about 98 per cent. The melted deposit tends to be of slightly lower fineness owing to impurities in the graphite if thin sheets of gold are deposited and split off, but the difference is slight (say 998 against 999) and is not perceptible in thick deposited sheets (from which the graphite has been scraped off), or in loosely adherent granules. In all cases the gold is perfectly malleable.

The possibility of using cathodes larger than the anodes is also one to be considered.

In any conclusions drawn from the summary of the various experiments given above, no dogmatic statements can be made, especially as the usual discussion on them cannot take place. My experiments were on a small, if in some respects an adequate, scale, with only a few ounces of gold in work. The summary may be taken as suggesting indications of lines along which it seems possible to make an advance.

#### *Relative Advantages of the Existing Methods of Refining.*

Little that is definite can be said on this subject. Ultimately everything depends on the relative cost, and it is to be recollected that refining is necessarily competitive and consequently that details as to the methods used in Europe and also the costs are not published. The advantages of the existing methods are sufficiently nearly balanced at present for the preference shown to one or other of them to depend largely on local conditions. Chlorine gas remains the predominant agent in Australia, electrolysis in America, and sulphuric acid in Europe.

The electrolytic method avoids acid fumes, and yields a pure product free from elements which cause brittleness. The refined gold is invariably tough and is well fitted for use in coinage or for the manufacture of wares. Gold from the chlorine process is of equal quality although a little lower in fineness, containing about 995 per 1000 of gold. Gold from the sulphuric acid process sometimes contains lead and probably tellurium and less reliance can be placed on its quality and fitness for use in coinage. Nevertheless, with care any difficulty from this source can be overcome, as has been proved by the experience in London. It may be recalled that the elements which interfere with the quality of gold in working are lead, bismuth, selenium, and tellurium, and, to a less extent, thallium, arsenic, and

antimony (*Thirty-third Annual Report of the Mint*, 1902, p. 73). Other elements, such as zinc, must be present in considerable proportion before any effect is caused. Silver and copper are harmless.

The working costs now amount to 2 cents or 3 cents per oz. of gold for the electrolytic process in the United States, as against 6 cents or 8 cents for the sulphuric acid process in the same establishments in the years 1900 to 1911, after allowing for the sale of the copper or bluestone (*Annual Reports of the Director of the U.S. Mint*). Moreover, the value of the platinum and palladium recovered in the electrolytic process is considerable (say, 0.5 cent per oz. of gold), whilst in the sulphuric acid process these metals are not recovered. Therefore, the statement made by Durham (*Trans. A.I.M.E.*, 1911, xlii., 374) and quoted by Gowland ("Non-Ferrous Metals," p. 290) that the electrolytic process is "more expensive" does not seem to be borne out by the Annual Reports of the Director of the United States Mints, if loss of interest is excluded.

On the other hand, in the sulphuric acid and chlorine gas processes, the gold is quickly brought to account and the difficulties of daily stocktaking are much less than in the electrolytic process. This is a serious point, as supervision must be very strict if it is impossible to weigh the gold in the refinery at the end of the day before the workmen leave.

Other disadvantages of the electrolytic process are given by Durham as "more care and intelligence required" and "losses liable to be greater." The actual losses are unknown as they are almost invariably more than covered by differences in assay, so that the refineries usually show a gain. This is a common feature of refineries, and one which excites the occasional wonder of gold miners. As for the "care and intelligence," this is a remark calculated to gratify those engaged in electrolytic refining, but may appear to the sulphuric acid refiners to be uncalled for. Some prudence is also required in dealing with boiling sulphuric acid.

The chief defect of the electrolytic process is the great length of the time of treatment as compared with the other processes, so that if the loss of interest on the gold is taken into account, a grave disadvantage is disclosed. Mr. B. P. Wirth, the Superintendent of the Melting and Refining Department of the New York Assay Office, writes to me in January, 1915, as follows:—

"The length of time necessary for the treatment of low grade gold in our refinery is from ten to twelve days. This includes alloying and melting into anodes, electrolysis in the silver cells, washing anode residue, re-melting into anodes for gold room, electrolysis in the gold cells, and washing and re-melting the fine gold." (Pulsating current used).

Dr. James Bonar (*Forty-fourth Annual Report of the Mint*, 1913, p. 177) observes that at Ottawa:—

"The average time needed, without night work, for the passing of rough gold through the silver cells and the gold cells till it is refined and ready for coinage is a little over three weeks, the greater part of the time being needed for the silver cells." (Direct current used).

According to Pearson (private communication, February, 1915), the work in the silver cells alone requires sixteen days at Ottawa.

Taking the total time of treatment from the importation of the gold into the refinery to its exportation, at a fortnight, and the gold locked up in the solutions, cathodes, connections, anode mud, &c., as 50 per cent. of the gold undergoing treatment, the interest charge at 5 per cent. would be about 6 cents per oz. of fine gold. It is obvious from such figures that if the gold undergoing treatment is losing interest, the work should be carried on for as many hours a day as possible with thin anodes and a high current density.

The use of silver strips and hangers instead of gold for the electrical connections and also of silver cathodes would reduce the amount of gold locked-up permanently, and

the average time of treatment has been reduced by the introduction of the pulsating current, which enables the treatment in the silver cells to be omitted in many cases. Nevertheless, there is still something to be desired in respect of the reduction of the loss of interest.

If the use of strong solutions of gold and hydrochloric acid with heavy currents as described above is found to be practicable, the electrolytic refiners could no longer be reproached for slowness. There seems some reason to hope that the anodes could be dissolved and the deposited gold washed and brought to account within the limits of a working day, and the difficulties of supervision thereby diminished.

At Ottawa the time of treatment is to be shortened and the silver cells dispensed with by means of a preliminary treatment with chlorine gas (Bonar, *loc. cit.*). In this way it is proposed to refine the gold up to 97 or 98 per cent and to finish by electrolysis. The chlorine plant has been installed, but full information with regard to its working is not yet available. In some trial runs, the gold was raised to 995 fine by chlorine and subsequently to 999.3 by electrolysis (Pearson, private communication, February, 1915). It remains to be seen whether the introduction of the chlorine process into the North American Continent will result in the total displacement of electrolytic refining there or in the confirmation of its presence. Up to now the chlorine process has not taken root anywhere outside Australia.

It is to be remembered that the electrolytic process was introduced to treat platiniferous gold and that in Germany it has always been doubted whether it can compete with sulphuric acid for any other purpose. This view falls to the ground if, for example, such material as Rand gold is classified as platiniferous. The matter is still undecided. It cannot yet be said which of the processes is destined to disappear before the competition of the others in the treatment of ordinary rough gold. Nevertheless I have been led to form the opinion, as the result of my study of the electrolytic process, that it will continue to be found useful.

The reluctance of a Government Department to accept new ideas caused the genius of Charles Watt to be wasted. Some respect has now been paid to his memory. Perhaps the highest form of recognition, that of the adoption of his proposals, will ultimately be accorded to him in his own country, as in other lands.

## ALCOHOL IN COMMERCE.

### RUSSIA OFFERS LARGE PRIZES FOR NEW INVENTIONS.

MANY people have been filled with wonder at Russia, a country in which an industry can be abolished at one word. The policy of the Russian Government, however, is not to abolish the alcohol industry but to direct it into useful channels. This is proved by a proclamation issued by the Ministry of Finance, details of which have just reached this country.

This proclamation should be of the highest interest to English chemists. It announces an international competition, in which many large prizes will be awarded, for the invention of a new denaturation process or the perfection of already existing processes to render impossible the use of alcohol as a drink, and for inventions to further the use of alcohol from a commercial point of view.

In the hope that the problems may be tackled to the advantage of English chemists we give below a translation of the main conditions of the competition.

#### Denaturation of Alcohol.

Three prizes of 30,000, 15,000, and 5000 roubles each will be awarded for the invention of denaturising substances fulfilling the following conditions:—

1. The substances must render alcohol totally unfit for use as a drink, by giving it a nauseous taste or by making

it repulsive to the organism by causing sickness or diarrhoea.

2. The substances must not emit an obnoxious smell which might render the use of alcohol unfit for commercial use.

3. The substances must not leave a residue after burning or contain anything harmful to apparatus in which the alcohol might be used.

4. It must be impossible to separate the denaturiser from the alcohol by any means whatever.

5. The raw material for the preparation of the denaturisers must be obtainable in sufficient quantities in Russia.

The specifications should be made out in French or Russian, and reach the Direction Générale des contributions indirectes et de la Régie de l'Alcool, Petrograd, before January 1, 1916.

The specifications should indicate the composition of the denaturiser, as well as the quantity required for each "vedro" (12.3 litres) of alcohol. These specifications, together with samples (not less than 1 kgm. each) of denaturisers, must be forwarded in a parcel bearing an identification mark. In a separate envelope bearing the same mark the name and address of competitor should be enclosed.

The judges may award the three prizes to the same competitor if his invention is of special merit.

The Government reserves to itself the right to use the denaturisers in respect of which prizes have been awarded without further indemnity.

#### Inventions for New Uses of Alcohol.

1. Three prizes of each 60,000, 30,000, and 10,000 roubles, for the invention of a new process for the use of alcohol in the manufacture of a produce which shall be, in nature, completely different to the alcohol used for its manufacture. For examples, ether, chloroform, &c., may be mentioned.

2. Three prizes, 50,000, 20,000, and 5000 roubles, for the invention of a new process for the use of alcohol in the preparation of a produce in which alcohol or its derivatives constitute one of the component parts of the said produce. It must be impossible to recover the alcohol from the produce in question. As examples, one may mention pharmaceutical preparations and scents.

3. Three prizes of 30,000, 15,000, and 5000 roubles for the invention of a new process to utilise alcohol in an industry in which alcohol or its derivatives would serve as intermediate and provisional solvent or as agent for precipitation. As an example, one may mention the production of smokeless powder and the manufacture of artificial silk.

The specifications should be sent as mentioned previously, and should include full description of the methods of usage as well as cost. The cost must be based on a price of 2 copeks per degree of alcohol (123 cc. of pure alcohol at a temperature of 15.5° C.).

Any samples sent must not be less than 1 kgm., and should any material used not be obtainable in Russia at least 5 kgms. must be sent in order to allow of trials being made.

The inventors shall reserve to themselves the right of exploitation, and letter patents shall be issued for the protection of their inventions.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 12th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir James George Frazer, Lady Frazer, and Mr. William Frederick Higgins were elected Members. The Honorary Secretary announced the decease of Prof. E. H. Amagat, Hon. F.R.S., and Geh. Regierungsrath Prof. Otto N. Witt, Ph.D., F.C.S., Honorary Members of the Royal Institution, and Resolutions of Condolence with the relatives were passed.



## PROCEEDINGS OF SOCIETIES.

INSTITUTION OF CHEMICAL TECHNOLOGISTS.  
(LONDON SECTION).

Colonel CHARLES E. CASSAL, V.D., President of the Institution, in the Chair.

## THE FUTURE OF BRITISH CHEMICAL INDUSTRY.

A SPECIAL Meeting of the London Section of the Institution was held on Thursday, March 11, 1915, at the Institution of Mechanical Engineers, Storey's Gate, St. James's Park, when the subject for discussion was "*The Future of British Chemical Industry*." The Discussion was opened by the President.

The PRESIDENT—Gentlemen, this is a meeting of the London Section of the Institution of Chemical Technologists. The Council of the Institution decided that in view of the importance of the subject to be discussed it was desirable to invite some gentlemen who are interested in that subject to attend the meeting. It is not a meeting of the Institution itself, but merely of the London Section called to discuss this question in the first instance, and with the view of preparing the way for a series of meetings in the future. The subject is so vast that it is quite impossible to discuss it in all its bearings at a single meeting of a section of this Institution, and the Council have felt that several meetings will probably be necessary before definite resolutions can be put forward, and before anything in the nature of final decisions can be arrived at. We have invited certain distinguished gentlemen to be present on this occasion, and we have received letters of a very encouraging nature from some of them who, unfortunately, have been prevented from attending; among them Mr. Bonar Law, Mr. Austen Chamberlain, the Earl of Denbigh, Lord Charles Beresford, and Captain Bathurst, M.P., who are all keenly interested in the objects of the Institution and in this meeting.

Before I proceed to open the discussion on the subject before the meeting I think it will be desirable that I should explain the position of the Institution of Chemical Technologists in regard to the matters which are to be discussed, and the reasons which have led the Council of the Institution to call this meeting together.

The Institution of Chemical Technologists was founded for the following purposes, among others:—

To advance the study and practice of technical chemistry, and to obtain for it the support and encouragement which from its importance to industry it deserves.

To effect the co-operation of professional chemists in all matters which may directly or indirectly promote the interests of their profession and its members.

To set up a high standard of professional conduct and responsibility.

To secure for technical chemists the effective expression of their due influence in all technical developments of chemistry both scientific and industrial.

To keep professional chemists in this country and in the Dominions in touch with each other for the discussion and treatment of all subjects of professional interest by means of District and Colonial Sections of the Institution, and through the medium of a journal and other literature devoted to the professional as well as to the scientific aspects of chemistry.

The part played by chemistry in the different departments of the public service and in relation to British industries is of such paramount national importance, and the responsibility attaching to the work of the scientific chemist is so heavy and extensive that, in the public interest, it has become a requirement of the utmost urgency to weld the various branches of the chemical profession together into a coherent whole. In order that the Nation may get the best value from the services rendered by them it is absolutely essential that all scientific chemists engaged in technical work should be linked together in

one professional body having a comprehensive membership and a definite policy, while the future of the profession and the maintenance of its position among the recognised professions depend entirely upon the co-operation of those who belong to it to advance its interests and to uphold its status—not merely for their own advantage but for the benefit of the country. The foundation of the Institution has met a public requirement of the highest importance in that one of its main objects is the unification and consolidation of the many different branches of the chemical profession, and it will be seen that the Institution is more comprehensive in its aims than all or any of the other chemical societies and institutions. Such good work as has been done and is being done by the older bodies referred to will be amplified and extended by the work of the Institution, which will endeavour to co-operate as far as possible with those bodies in the development of the work that they are doing. A consideration of the functions fulfilled by the four other chief chemical institutions in this country will show at once that those bodies do not and cannot aim at the objects which the Institution of Chemical Technologists is endeavouring to attain, and that their work in no way clashes with that of the Institution. The Chemical Society of London—the oldest of the bodies in question—is concerned practically entirely with theoretical chemistry—work undoubtedly of the greatest importance, but the prosecution of which precludes the possibility of paying adequate attention to applied and technical chemistry, or of affording encouragement and support to these branches of science. The Institute of Chemistry of Great Britain and Ireland is mainly, if not practically entirely, an examining body, the diplomas of the Institute being ordinarily granted only to those who have gone through certain specified courses of study and training, and who have passed the examinations conducted by the Institute. Owing to the imposition of several somewhat narrow restrictions which are distinctly out of date, the membership of the Institute is necessarily open only to a comparatively small number of the many hundreds of professional chemists actually engaged in the various branches of chemical practice. The "Society of Public Analysts and other Analytical Chemists" is practically confined to persons who are directly or indirectly concerned with analytical chemistry, and the activities of the society are restricted to the reading of papers on analytical subjects and the publication of an analytical journal—the *Analyst*. The Society of Chemical Industry is mainly concerned with chemical manufacture from the present unfortunately restricted point of view of the ordinary British manufacturer. By the publication of its journal and in other ways, this society has certainly done excellent work. Unfortunately, however, the membership is not confined to professional chemists, and, still more unfortunately, is not confined to British subjects—a circumstance which, in the opinion of those qualified to judge—has been, and is, not only highly dangerous, but probably extremely injurious to the interests of British chemical industry, and, in consequence to the country. It must be borne in mind that there are a great many professional chemists actively engaged in most important work in connection with our chemical industries who do not belong to any of the bodies referred to, and it is the business of the Institution of Chemical Technologists to collect these isolated and unquestionably valuable elements and to place them in their proper places in an organised body. The chemical profession stands alone among the professions in that it is utterly without organisation, and in that it is split up into a number of different camps. The fellowship and the power of united action which must be created in this profession as it was created in the professions of medicine and law, and in others, to the advantage of those professions as well as to the advantage of the public, that fellowship and power of united action which should result from a common training, and from the recognition of a common end to be attained, can only be brought about by the activity of a broadly-based institution

ree from the trammels which hamper the operations of older bodies constituted when the needs of to-day did not exist. If industrial success is to be secured, and if it is to be made permanent, adequate inducements must be offered to men of capacity and ability to adopt applied chemistry as a profession. One of the first steps necessary is the establishment of professional unity and the power to ensure the effective recognition of the profession upon which our industrial success in the future entirely depends.

At the present time there is no relationship, nor is there any sympathy between the college laboratory and the technical laboratory, and it is essential that intimate relations between the two should be brought into existence. The arbitrary and false distinction, which if not actually expressed in words exists in fact, between so called "pure" chemistry and applied chemistry, to the undue exaltation of the former at the expense of the latter, must be abolished. Applied science is no whit inferior to that which is called "pure" science, and the followers of each should be sufficiently intelligent and broad minded to recognise the value of each other's work, and to remember that both are members of a great profession. The "pure" chemist, he who has the responsibility of teaching the future members of his profession in the colleges, must be brought to recognise the unity of pure and applied chemistry and that the one is in no way inferior as an intellectual pursuit to the other. At present no such unity is recognised. The colleges are the breeding grounds for the scientific industrial advisers of the future, but the breeding ground is not enough, and the production of the skilled and sound scientific adviser from the college trained man can only be secured by his absorption of the knowledge and experience alone obtainable by actual and active practice in the professional or technical laboratory, and, when industrial processes are concerned in the works themselves. This, a matter of vital importance, is very far from being generally recognised. It is on the unity and efficiency of the chemical profession that the future success of British chemical industry must, in the first instance, necessarily depend, and in this connection it is safe to say that the synthetic production of dyes and drugs and the manufacture of so-called "fine chemicals" would never have passed from our hands into those of the most despicable nation on earth if intelligent and effective relations between the college and the works had been initiated and fostered, if in past years our more brilliant students had been encouraged by their College teachers to devote themselves to Technical Chemistry, and if our manufacturers had been shaken out of their ignorance and apathy, taught to appreciate the value of scientific research, and led to recognise the absolute necessity of highly skilled advice for the maintenance and prosperity of their concerns. Had these conditions obtained and had the legislature through the influence of a united profession been forced to appreciate the value of Science, so long and so shamefully neglected by the State in its ignorance and ineptitude, the industries now practically entirely in foreign hands would have been in ours, to the benefit of the manufacturers, of other industries, and of many thousands of workers. Wrapped in slumber, or wasting their time in futile political bickerings and quarrels of the "parish pump" order, the British people for years past have been oblivious to the problems which really bear on their own vital interests and have allowed themselves to be robbed of the fruits which should have been theirs.

While the sins of omission and commission, past and present, which have been committed by all concerned in varying degrees—by our Legislature, our Governments, our manufacturers, and by the members of the chemical profession themselves—must make the angels weep, those of us who know must leave the weeping to the angels and face the future with the determination to work for the fundamental alteration of existing conditions and the inauguration of a new era. "Wake up, England!" the warning cry of our present King, amply justified as it was at the time that it was uttered, is more than ever justified

to day. There has been a rude awakening indeed, but the sleep has not yet gone completely from the eyes of our people, and the hour has come to make the awakening thorough. I ask this meeting to ponder on the causes which have brought about the loss of our former leading position in chemical industry, and to consider the main directions in which immediate reform is needed.

(To be continued)

## ALCHEMICAL SOCIETY

### *Alchemy and Phallicism.*

THE nineteenth General Meeting of the Alchemical Society was held at 7.30 p.m. on Friday, April 9, at 1, Piccadilly Place, Piccadilly, W. The chair was occupied by Mr. ARTHUR EDWARD WAITE and a paper entitled "*The Phallic Element in Alchemical Doctrine*" was read by the Acting President (Mr. H. STANLEY REDGROVE, B.Sc. Lond., F.C.S., author of "Alchemy: Ancient and Modern," &c.). The lecturer commenced his most interesting discourse by bringing forward further evidence in support of his theory that the doctrines of the medieval alchemists originated in an attempt to apply by means of analogy the accepted religious dogmas concerning the soul and its destiny to chemical and physical phenomena. A further source of *a priori* reasoning was, the lecturer said, to be found in the rudimentary physiology of the period. It was natural for primitive man to attempt to explain the universe anthropomorphically, and this led to his attributing sex not only to the world as a whole but to inanimate objects. This gave rise to phallicism, or the worship of sex, and so far as the alchemists were concerned, what the lecturer called "the phallic element in alchemical doctrine" manifested itself in a belief that the metals propagated themselves sexually by means of seed, and in many other curious views which he discussed in detail. He gave evidence for believing, however, that the alchemists' debt to theology was a greater and more fundamental one than that to phallicism, important though this latter debt undoubtedly was.

In conclusion, Mr. Redgrove briefly dealt with the significance of sex for alchemy understood as a mystical process carried out on man himself, in which sense, as he pointed out, it appears to have been understood by a few transcendental alchemists of the sixteenth and seventeenth centuries.

The lecture was followed by an animated discussion. The full text will be published in the April issue of the Society's *Journal*.

## NOTICES OF BOOKS.

*Soil Condition and Plant Growth.* By EDWARD J. RUSSELL, D.Sc. (Lond.) New Edition. London, New York, Bombay, Calcutta, and Madras: Longmans Green, and Co. 1914.

In the third edition of this book, which belongs to the series of monographs on biochemistry edited by Drs. Plimmer and Hopkins, a new chapter has been added on the relation between the micro-organic population of the soil and the growth of plants, in which a comprehensive account is given of the organisms which act directly or indirectly on the plant, and the nature of their action. Other new sections have been added, and the latest results of investigations incorporated in the text. The author always gives a very fair view of the theories advocated by the workers of all schools. The interpretation of soil analysis is well treated, and an appendix contains brief descriptions of the most generally adopted methods of analysing soils.

**Leavening Agents.** By RICHARD N. HART, B.S. Easton, Pa.: The Chemical Publishing Co. 1914.

THIS book is intended to provide bakers with full and at the same time concise information about the chemistry and technology of baking-powder and aerating agents generally. A detailed account of the manufacture of yeast is included, and practical directions are given for the preparation of home-made yeast and leavens. The literature of the subject appears to have been systematically and thoroughly searched, and the section on baking-powders gives a clear summary of the difference in constitution and properties of cream of tartar and alum powders. The volume includes short chapters on the manufacture of aerated bread, and the preparation of milk powder.

**Bulletin of the Imperial Institute.** Vol. XII., No. 4.

THIS number of the *Bulletin of the Imperial Institute* contains some particularly interesting articles, which deserve the careful attention of those who are interested in the development of the resources of the British Empire. Some information is given as to the Technical Information Bureau, which was established at a very opportune moment and which has now been doing valuable work for some months. For example, it has collected data relating to the world's resources of potash and has published details of the German palm kernel industry. The present number of the *Bulletin* contains a comprehensive article on the use and value of copra as a feeding-stuff, and another on the present scarcity of antiseptic thymol, in which the possibilities of preparing it in England, or carvacrol as a substitute for it, are discussed.

## CORRESPONDENCE.

### CHLOROPHYLL GREEN.

*To the Editor of the Chemical News.*

SIR,—I have discovered a cheap method of making chlorophyll green.

Like the chlorophyll of the text-books it is soluble in alcohol, but not in oils or water.

Yet, commercially, this article is obtainable soluble in any one of these. Can any correspondent tell me how this is done?—I am, &c.,

C. W. B. SHORTO.

## MISCELLANEOUS.

The Supply of Sulphuric Acid for Government Contractors.—In view of the importance of sulphuric acid in the manufacture of materials required for Government purposes, an Advisory Committee has been appointed in connection with the High Explosives Department of the War Office to assist in ensuring an adequate supply of acid to Government contractors. All communications on this subject should be addressed to The Secretary, War Office High Explosives Department (A. 6), Storey's Gate, S.W.

Determination of Small Quantities of Boric Acid.—G. Halphen.—A solution of turmeric is prepared by shaking 2 grms. of the powdered root with 100 cc. of acetic ether. The boric acid is separated as sodium salt from the substances to be tested (Bertrand and Aquilon's method). The methylboric ether is received in 0.2 cc. of normal soda, and the solution is concentrated and then evaporated to dryness. The residue is taken up with 1 cc. of water to 2 cc. of HCl, and simultaneously comparison solutions are made all containing in 1 cc. of liquid 0.2 cc. of soda and increasing quantities of boric acid; e.g., 0.0088 mgrm., 0.0177 mgrm., 0.0265 to 0.088 mgrm. By comparing the colours it is possible to determine the amount of boric acid to within 8 thousandths of a mgrm. of boron.—*Annales des Falsifications*, No. 75, 1915.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers

Great George Street, Westminster, on Thursday and Friday, May 13 and 14, 1915, commencing each day at 10.30 o'clock a.m. The following programme has been arranged:—

**Thursday, May 13—**

10.30 a.m.—General Meeting of Members. The Bessemer Gold Medal for 1915 which has been awarded to Mr. Pierre Martin (formerly of Sireuil, near Paris) will be received on his behalf by His Excellency M. Paul Cambon, the French Ambassador, who has kindly consented to attend. A selection of papers will be read and discussed.

3.0 p.m.—Lecture by Prof. Hubert (Liège University) on "Large Gas Engines."

**Friday, May 14—**

10.30 a.m.—General Meeting of Members. The Andrew Carnegie Gold Medal (for 1914) will be presented to Mr. E. Nusbaumer (Paris), and the award of Research Scholarships for the current year will be announced. A selection of papers will be read and discussed.

The following is a list of papers that are expected to be submitted for reading and discussion:—

F. W. Adams—"Diffusion of Carbon in Iron."

J. O. Arnold and G. R. Bolsover—"Supplementary Notes on the Forms in which Sulphides may exist in Steel Ingots" (Part II.).

G. Charpy and A. Cornu—"Researches on Iron, Silicon, and Carbon Alloys."

J. A. Newton Friend and P. C. Barnett—"Corrosion of Iron in Aqueous Solutions of Inorganic Salts."

J. A. Newton Friend and C. W. Marshall—(a) "Relative Corrodibilities of Grey Cast-iron and Steel"; (b) "Note on the Removal of Rust by means of Chemical Reagents."

A. Greiner—"The Heating of an Open-hearth Furnace by means of Tar."

Sir R. A. Hadfield and G. K. Burgess—"Sound Steel Ingots and Rails."

K. Honda—"Nature of the  $A_2$  Transformation in Iron."

A. McWilliam and E. J. Barnes—"Brinell Hardness and Tenacity Factors of a Series of Heat-treated Special Steels."

A. M. Portevin and E. L. Dupuy—"Thermo-electric Properties of Special Steels."

J. H. Smith and G. A. Wedgwood—"Stress-strain Loops for Steel in the Cyclic State."

J. E. Stead—"Detection of Burning in Steel," and "Iron, Carbon, and Phosphorus."

**Annual Dinner.**—The Council have decided, that on account of the war, it will be inadvisable to hold the Annual Dinner this year.

**Autumn Meeting.**—It has been provisionally decided that the Autumn Meeting shall be held in London during the week ending September 25.

## MEETINGS FOR THE WEEK.

MONDAY, 26th.—Royal Society of Arts, 8. (Cantor Lecture) "Food stuffs," by David Sommerville, B.A., M.D.

TUESDAY, 27th.—Royal Institution, 3. "The War on Belgians Architecture," by Banister Fletcher, F.R.I.B.A.

WEDNESDAY, 28th.—Royal Society of Arts, 5.30. "Utilisation of Solar Energy," by A. S. E. Ackermann, D.Sc.

THURSDAY, 29th.—Royal Institution, 3. "Advances in General Physics," by Dr. A. W. Porter, F.R.S.

— Royal Society. "Transmission of Infra-red Rays by the Media of the Eye, the Transmission of Radiant Energy by Crookes's and other Glasses, and the Radiation from various Light Sources," by H. Hertridge and A. V. Hill. "Surface Tension and Ferment Action," by E. Beard and W. Cramer. "Surface Tension as a Factor controlling all Metabolism," by W. Cramer.

FRIDAY, 30th.—Royal Institution, 9. "Emulsions and Emulsification (Experimental)," by F. G. Donnan, F.R.S.

— Institute of Petroleum Technologists, 8. "Oil Well Engineering," by W. Calder.

SATURDAY, May 1.—Royal Institution, 3. "Photo-Electricity (Experimental)," by Prof. J. A. Fleming, F.R.S.

— Royal Institution, 5. Annual Meeting.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2892.

## THE RELATION OF SCIENCE TO THE STATE.

AT no period in the history of the world has the need for the complete readjustment of men's ideas been so overwhelmingly insistent as at the present moment, when the whole of civilisation appears to have been put into the melting pot, and no one knows what may emerge thence. New problems and new theories are being forced upon us from all sides, and thinking men realise that our first task is the stupendous one of overcoming the inertia of inherent conservatism and opposition to radical changes in valuations and habits of thought. It is of the utmost importance that we should endeavour to begin betimes our readjustment of ideas and practice, and no subject needs more careful consideration and clear thinking than the relation between science and the State. Men's minds are full of modernities, problems of new methods of warfare, new kinds of equipment, and the utilisation of new resources, and perhaps they have never before, consciously or unconsciously, been so open to receive new ideas. Many necessary experiments and changes have been made, without, as far as one can see, any of the dire consequences frequently foretold by prophets of evil, and there is hope that others more drastic and far-reaching may be attempted, and reforms which have long been urgently needed may at last be effected. Scientific men would be lacking in a sense of duty and responsibility if they did not seize the opportunity of calling attention to the supreme importance to the nation of the cultivation of the scientific habit of mind and of the right attitude towards scientific work of all kinds. As a nation we have undoubtedly made grievous mistakes in the past, but signs are not wanting that we are becoming more ready to benefit by experience and to learn from our mistakes. Not the least of our national errors has been our neglect of science, we might almost say our disparagement of scientific achievements and our lack of foresight in fostering the spirit of research. It is to be hoped that we shall at last learn our lesson and profit not only by our own mistakes but also by those of our friends and enemies alike.

The duty of science to the State is two-fold. Science ought to be ready to give her services freely, and this duty has never been shirked. The Royal Society, for example, has willingly put at the disposal of the Government the knowledge and advice of experts in all branches, without remuneration or reward. Scientific men cannot be said to have neglected their duties in this respect, nor to have shown any reluctance to give of their best to the nation. The general public, while perhaps not realising the magnitude of their debt to science, have been eager to take advantage of the applications of scientific knowledge, and while the practical outcomes of such knowledge are fully appreciated and extolled, the value of the spade work which has been done, and which must continue to be done, by men who may perhaps remain almost unknown to the world at large is quite unrecognised. It needs some knowledge and a good deal of imagination to realise the importance of research work when its immediate applications are not apparent, and the second duty of scientific men is undoubtedly to educate public opinion on the subject—a duty which is by no means generally appreciated. The classically-trained statesman of to-day, who would, for example, probably be able to state clearly some of his views on the debt the world owes to Shakespeare, but on the other hand would in all probability be quite unashamed to admit that his knowledge of the achievements of Faraday was almost non-existent,

accepts as a right the gifts that science has bestowed freely upon civilisation, while at the same time slightly despising the rank and file at any rate of the workers who have prepared the way for discoveries and inventions. The general public follows the lead given to them, grudges money to be spent on the endowment of science, and acquiesces in its starvation for want of funds. This is more particularly the case in reference to the allocation of money to or the encouragement of research in pure science. Half-hearted attempts have been made to foster the spirit of research, as, for example, the granting of the lower University degrees chiefly for original work. This is, however, certainly beginning at the wrong end, and cannot be viewed as an altogether satisfactory experiment. Research founded on incomplete knowledge is worse than useless, and the setting of very young and only partially trained men upon original investigation is justified only in exceptional cases. On the other hand, what would appear to be a wiser scheme would be the provision of a liberal scientific education, begun at the school and continued by specialisation in the excellent laboratories and under the teachers who are doing valuable work at our Universities. On the completion of his University career the student should be given the opportunity, either on the recommendation of his teachers, or by competitive or other examination, of obtaining employment as a researcher at properly equipped research institutes. It is at present by no means easy for a science graduate to obtain remunerative work, other than teaching, immediately upon leaving college, and it is recognised that the teaching profession absorbs a good many men whose energies would be more profitable if they were engaged in some other pursuit. While it is undoubtedly true that the good teacher must possess something of the spirit of the researcher the converse does not always hold good—it is only necessary to call to mind the spirit of self-assertion and the power of insight into character which are indispensable in the teacher. The opportunity of adopting another career in which the prospects of advancement were good and the remuneration commensurate with that obtained by teaching would be eagerly welcomed by many students. The research institutes could be directed by men of eminence in their own branches, who, freed from the need of performing professorial duties, could give up their time to research and to advising the junior members of the staff. As a branch of the Civil Service the research institutes would be doing work of inestimable value to the nation, and would provide a source of thoroughly well-trained men who had proved themselves to have the ability of the special kind needful for successful research work. There would no longer be any need for trying to induce Germans to come to England to direct English scientific enterprises, nor any excuse for the employment in our works' laboratories of German chemists or managers.

In return for its services to the State science has a right to look for more recognition on the part of the Government, greater scope for its activities, and more prospects of obtaining good remuneration, so that the scientific man may be able to pursue his work free from anxiety about ways and means for himself and his dependents.

The lessons the nation has to learn in this time of discipline and stress are many and of vast importance. We cannot but plead guilty to the charge of an inordinate love of money which has led us into extravagances of luxury and indirectly has exaggerated our spirit of utilitarianism. It has always been exceedingly difficult to interest the public in any scientific work the practical application and utility of which are not apparent. The British are by no means inferior to Continental nations in originality of mind and intellectual initiative, but the desire for immediate practical returns has led to the neglect of work which in itself and at first sight has appeared to be incapable of useful application. Insight and faith have been lacking, and we have not learnt by experience, as we should, that abstract research, undertaken without any

definite practical aim in view, is an absolutely necessary preliminary to all scientific discoveries. Although it is perhaps not difficult to criticise the quality of some of the German research work in chemistry for example, we must admit that the quality produced is enormously greater than that emanating from British Universities. The German scientific societies publish a much greater amount of original work than the British societies, and although some of it may appear to be unimaginative and inferior in value, the quantity of it is a measure of the distribution throughout the nation of the research spirit. The results of the German methods of scientific education have certainly been the production of men of resource, who are able to act promptly and on their own initiative in emergency, such as we appear to lack at the present crisis. In the future we shall perhaps prove more ready to learn from our neighbours, rejecting as well as accepting their ideas, and observing their mistakes as well as their successes, and although the correction of national faults is necessarily a slow process, it is perhaps not too much to hope that now England will really begin to wake up and no longer be content to be outclassed in the future as she has been in the past, owing to the mistaken policy and supineness of her statesmen and educationalists and to the insularity of her people.

#### A NEW METHOD FOR THE ANALYSIS OF THE COPPER AND TIN GROUPS.

By ROBERT GILMOUR.

THE qualitative separation of the metals of the copper and tin groups has always been a matter of some difficulty, and no method of effecting the separation has been devised which can claim to be entirely satisfactory.

The usual method of procedure is to separate the copper and tin groups by means of yellow ammonium sulphide, but this reagent often fails to dissolve stannous sulphide completely, and has other well known disadvantages which would quickly lead to its abandonment if a satisfactory method of analysis could be devised which did not involve its use.

Until recently the only method involving the use of the caustic alkalis was that due to J. Walker (*Journ. Chem. Soc.*, 1903, lxxxiii., 184), who employed sodium hydroxide with the addition of a little yellow ammonium sulphide, to oxidise any stannous tin present. Sodium peroxide was then added to reprecipitate any mercuric sulphide which had been dissolved. This method, however, is occasionally troublesome owing to the fact that insoluble sodium pyroantimoniate is formed. A modification of the method is sometimes used in which the addition of sodium peroxide is omitted, but in this case, quite apart from the mercuric sulphide which is dissolved, considerable quantities of stannous sulphide may escape solution, and furthermore, as Curtman and Marcus have shown (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 1093), arsenious and antimonious sulphides, when heated with sodium hydroxide in the presence of stannous sulphide, are partially reduced to the metallic state.

In the paper by Curtman and Marcus, which is quoted above, a method of separation is proposed in which sulphur dioxide is made use of to oxidise any stannous tin to stannic before the precipitation of the copper and tin groups with sulphuretted hydrogen. This method necessitates the removal of the alkaline earth metals as sulphates before treatment with sulphur dioxide, and to some extent renders the course of the analysis unnecessarily complex for ordinary purposes.

In the case of the copper group itself the use of nitric acid to separate mercuric sulphide has certain disadvantages, and the separation of lead and bismuth is frequently troublesome. Lead if present in only small quantities is easily overlooked if precipitated as sulphate, and unless

special precautions are taken it is difficult to remove completely, with the result that complications may arise when testing for bismuth.

The method of separation about to be described appears to avoid most of the usual difficulties, and the fact that no use is made of reagents like sulphur dioxide or ammonium sulphide seems to make it a method worthy of general use.

Briefly the procedure is as follows:—The metals of Group II. are precipitated as usual with  $H_2S$ . The sulphides are treated with boiling 5/N HCl, which decomposes them all with the exception of  $HgS$ ,  $CuS$ , and  $As_2S_3$ . The arsenious sulphide is then separated by extracting the residue with NaOH. The filtrate containing the remaining metals of the group is boiled to remove  $H_2S$ , 15 to 20 cc. of  $H_2O_2$  is added, and the mixture evaporated almost to dryness to remove excess of acid. Any stannous tin is in this way oxidised to the stannic condition. The residue is dissolved in water and the metals again precipitated as sulphides.  $Sb_2S_3$  and  $SnS_2$  are then removed by extraction with NaOH. In separating bismuth and lead advantage is taken of the insolubility of bismuth dichromate in NaOH and the solubility of lead chromate in this reagent.

#### Preliminary Experiments.

1. (a) Freshly precipitated  $Bi_2S_3$  was treated with boiling 2/N HCl. The greater part seemed to go into solution quickly, but a residue remained which only dissolved on boiling for some time. This suggests the presence of different forms of the sulphide analogous to those of nickel (*Zeit. Anorg. Chem.*, 1914, lxxxvi., i.). (b) When boiled with 3·3/N HCl  $Bi_2S_3$  dissolved completely and in a few moments.

2. Freshly precipitated  $Sb_2S_3$  was treated with 3·3/N HCl, but even on prolonged boiling did not dissolve completely. On the other hand, with boiling 5/N HCl complete solution was effected in a few moments.

3. Freshly precipitated  $HgS$  and  $CuS$  were treated with 5/N HCl at the boiling-point for two minutes.  $H_2S$  was passed into the hot mixture for a minute. On filtering, diluting the filtrate largely and saturating it with  $H_2S$ , no precipitate was obtained.  $HgS$  and  $CuS$  are therefore not attacked by 5/N HCl under these conditions.

100 mgrms. of  $As_2S_3$  were treated with 5/N HCl, and the cold mixture saturated with  $H_2S$ . The mixture was boiled briskly for two minutes and filtered. On passing  $H_2S$  into the filtrate a small precipitate of 1 to 2 mgrms.  $As_2S_3$  was obtained.

1 mgrm. of  $As_2S_3$  was treated in the same manner. The filtrate on saturating with  $H_2S$  gave practically no indications of the presence of As, or, at least, only an extremely slight yellow turbidity.

In a parallel experiment 100 mgrms. of  $As_2S_3$  were boiled with 5/N HCl for two minutes without previously saturating the mixture with  $H_2S$ . The filtrate on treatment with  $H_2S$  gave a precipitate of  $As_2S_3$  of 5 to 10 mgrms.

The other sulphides of the group when mixed with 5/N HCl saturated with  $H_2S$  dissolved easily on boiling.

4. A solution containing 200 mgrms. of Sb in 10 cc. of 5/N HCl was heated to boiling and the hot solution saturated with  $H_2S$ . No precipitate appeared. On cooling the solution under the tap an immediate bright red precipitate of  $Sb_2S_3$  was obtained.

Under the same conditions 1 mgrm. of Sb gave on cooling no precipitate, but on adding 2 cc. of water and shaking a pale red precipitate appeared, which increased in quantity on keeping the solution under the tap.

A similar test with 0·2 mgrm. of Sb in 10 cc. of 5/N HCl gave after cooling, adding 2 to 3 cc. of water, and further cooling, a distinct pale yellow turbidity. In all cases the precipitates of  $Sb_2S_3$  dissolved on heating, but reappeared on cooling the solution under the tap.

5. An exactly similar experiment, in which 250 mgrms. of [Sn(ic) tin were used, gave no precipitate on cooling,



but on diluting largely a yellow precipitate of  $\text{SnS}_2$  was obtained.

A solution containing 250 mgrms. of  $\text{Sn(II)}$  tin and 1 mgrm. of  $\text{Sb}$  gave the above mentioned test for  $\text{Sb}$  quite easily.

6. A solution containing 100 mgrms.  $\text{Sb}$  in 20 cc. of 3·3  $\text{N HCl}$  1 vol.  $\text{HCl}$  (1·16) + 2 vols.  $\text{H}_2\text{O}$ —was heated to boiling and saturated with  $\text{H}_2\text{S}$ . The antimony was precipitated completely as  $\text{Sb}_2\text{S}_3$ . The filtrate on diluting largely gave no further precipitate with  $\text{H}_2\text{S}$ .

A similar solution containing 100 mgrms. of bismuth in 20 cc. of 3·3  $\text{N HCl}$  was heated to boiling and treated with  $\text{H}_2\text{S}$ . No precipitate appeared. On cooling under the tap a black precipitate of  $\text{Bi}_2\text{S}_3$  immediately appeared. A precipitate of  $\text{Bi}_2\text{S}_3$  was also obtained when a few drops of water were added to the hot solution.

A solution containing 50 mgrms. of antimony and 50 mgrms. of bismuth in 20 cc. of 3·3  $\text{N HCl}$  was heated to the boiling-point and saturated with  $\text{H}_2\text{S}$ . A pure red precipitate of  $\text{Sb}_2\text{S}_3$  was obtained, and on filtering and diluting the filtrate a black precipitate of  $\text{Bi}_2\text{S}_3$  came down.

The metals  $\text{Bi}$  and  $\text{Sb}$  can thus be separated if care be taken to keep the liquid near the boiling-point and to filter through a dry filter-paper into a dry vessel. The precipitate or  $\text{Sb}_2\text{S}_3$  should then be washed with hot 3·3  $\text{N HCl}$ , containing  $\text{H}_2\text{S}$ , before washing with water, in order to prevent any precipitation of bismuth through local dilution of the acid solution.

7. The above experiments show that a separation of mercury, copper, and arsenic from the other members of the group can be effected by boiling the mixed sulphides with 5  $\text{N HCl}$  which has been saturated with  $\text{H}_2\text{S}$ . Any trace of  $\text{As}$ , which may be dissolved, can be removed by passing  $\text{H}_2\text{S}$  through the filtrate at the boiling-point.

The filtration must be carried out while the solution is just slightly below the boiling-point, and it is advisable to use a dry filter-paper in a funnel which has been warmed by pouring boiling water through it. Under these conditions no precipitation of  $\text{Sb}_2\text{S}_3$ , due to cooling or local dilution of the acid solution, need be feared.

8. 100 mgrms. of bismuth as chloride and 10 mgrms. of lead as nitrate were precipitated by  $\text{NH}_4\text{OH}$ , and the precipitated hydroxides washed; they were then dissolved up in a few cc. of hot 2  $\text{N HNO}_3$ . To the solution  $\text{K}_2\text{CrO}_4$  was added, then  $\text{NaOH}$  in excess, and the mixture boiled for a moment and filtered. The filtrate was acidified with acetic acid. An immediate yellow precipitate of  $\text{PbCrO}_4$  was obtained, which dissolved on making the solution alkaline with  $\text{NaOH}$ . The yellow residue on the filter, consisting of bismuth dichromate, was dissolved in a little dilute  $\text{HCl}$ . On adding sodium stannite the characteristic black precipitate of bismuth was obtained.

A similar experiment with 50 mgrms. of bismuth and 1 mgrm. of lead gave a very pronounced yellow turbidity of  $\text{PbCrO}_4$ , while a blank experiment consisting only of bismuth gave no trace of a turbidity on acidifying with acetic acid.

(NOTE.—The  $\text{HCl}$  used throughout these experiments had a specific gravity of 1·165 and a strength of approximately 10 times normal. The 5  $\text{N}$  acid referred to was obtained by adding an equal volume of water to the concentrated acid and the 3·3  $\text{N}$  by adding 2 vols. of water).

#### *Copper and Tin Group.*

*Separation of Hg, Cu, Pb, Bi, Cd, As, Sb, and Sn.*—Precipitate the metals of the group in the usual way, and wash with warm  $\text{H}_2\text{S}$  water containing a little  $\text{NH}_4\text{Cl}$ .

*Filtrate.*—Group III.

*Precipitate.*—Sulphides of  $\text{Hg}$ ,  $\text{Cu}$ ,  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cd}$ ,  $\text{As}$ ,  $\text{Sb}$ , and  $\text{Sn}$ . Transfer the sulphides to a small beaker, add 30 cc. of 5  $\text{N HCl}$ —1 vol. conc.  $\text{HCl}$  (1·16) + 1 vol. water—pass  $\text{H}_2\text{S}$  gas through the mixture for one minute, heat to boiling, and keep at this temperature for two minutes. Filter through a dry filter-paper in a funnel which has been warmed with hot water; wash the residue

with a few cc. of warm 5  $\text{N HCl}$ . Heat the filtrate again to boiling, and treat with  $\text{H}_2\text{S}$  gas for a few moments, to remove any traces of arsenic which may have been dissolved by the  $\text{HCl}$ , and filter again as before. Combine the residues.

(NOTE.—The filtration must be carried out while the liquid is still very hot, and local dilution of the acid through contact with a wet filter-paper is to be avoided, otherwise antimony if present in any quantity will be precipitated to some extent—see Preliminary Expt. 5).

*Residue, R<sub>1</sub>.*— $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{As}_2\text{S}_3$  (trace  $\text{Sb}_2\text{S}_3$ ).

Boil the precipitate with about 10 cc. of  $\text{NaOH}$  solution (2  $\text{N}$ ) for a few moments, filter, and wash.

*Residue, R<sub>2</sub>.*— $\text{HgS}$ ,  $\text{CuS}$ .

Dissolve in a few cc. of  $\text{HCl}$  (conc.) with the addition of a few crystals of  $\text{KClO}_3$ . Evaporate almost to dryness, and dilute to about 5 cc. Test a portion of the solution for  $\text{Hg}$  with  $\text{SnCl}_2$ , and another portion for  $\text{Cu}$  with  $\text{K}_4\text{Fe(CN)}_6$ .

*Filtrate, F<sub>2</sub>.*— $\text{Na}_3\text{AsO}_3$  and  $\text{Na}_3\text{AsS}_3$ .

Add a few cc. of  $\text{H}_2\text{O}_2$  solution and boil. (Any black precipitate which may form is filtered off and tested for  $\text{Hg}$ ). Continue the boiling for a few moments to destroy excess of  $\text{H}_2\text{O}_2$ ; neutralise with  $\text{HCl}$ , and to the solution add its own volume of  $\text{HCl}$  (conc.). Heat to boiling, and saturate with  $\text{H}_2\text{S}$ . A yellow precipitate denotes  $\text{As}$ .

(NOTE.—On filtering off the  $\text{As}_2\text{S}_3$ , cooling the filtrate under the tap, and diluting, a small orange precipitate or turbidity due to  $\text{Sb}_2\text{S}_3$  is always obtained here if the substance under examination contains this element).

*Filtrate, F<sub>1</sub>.*—Chlorides of  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cd}$ ,  $\text{Sb}$ , and  $\text{Sn}$ .

Boil to expel  $\text{H}_2\text{S}$ , add 15 cc.  $\text{H}_2\text{O}_2$ , and evaporate almost to dryness. Dissolve the residue in 20 cc. of water with the addition of 4 to 5 cc. dilute  $\text{HCl}$  (2  $\text{N}$ ). Heat to boiling, and saturate with  $\text{H}_2\text{S}$  gas. Dilute to 50 cc., and again saturate with  $\text{H}_2\text{S}$ . Filter, and wash.

*Precipitate, P<sub>2</sub>.*—Sulphides of  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cd}$ ,  $\text{Sb}$ , and  $\text{Sn(II)}$ .

Boil with 10 cc. of  $\text{NaOH}$  (2  $\text{N}$ ) for a minute or two. Filter, and wash.

*Residue, R<sub>3</sub>.*—Sulphides of  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cd}$ .

Dissolve in a little (5 cc.) hot 3·3  $\text{N HCl}$  (1 vol. conc.  $\text{HCl}$  + 2 vol.  $\text{H}_2\text{O}$ ). Add  $\text{NH}_4\text{OH}$  in excess, boil, filter, and wash.

*Precipitate, P<sub>3</sub>.*— $\text{Bi(OH)}_3$ ,  $\text{Pb(OH)}_2$ .

Dissolve in 3 to 4 cc. boiling dilute (2  $\text{N}$ )  $\text{HNO}_3$ . (Pour the acid through the filter several times). Add 5 cc. of  $\text{K}_2\text{CrO}_4$  solution and 10 cc.  $\text{NaOH}$ . Heat to boiling, and filter.

*Residue, R<sub>4</sub>.*— $(\text{BiO})_2\text{Cr}_2\text{O}_7$ .

Add a few cc. of dilute  $\text{HCl}$  to the precipitate, and filter into a solution of  $\text{Na}$  stannite. A black precipitate or coloration indicates  $\text{Bi}$ . Acidify the filtrate containing  $\text{Na}_2\text{PbO}_2$  +  $\text{K}_2\text{CrO}_4$  with acetic acid. A yellow turbidity or precipitate of  $\text{PbCrO}_4$ , which dissolves up again on making alkaline with  $\text{NaOH}$ , indicates  $\text{Pb}$ .

*Filtrate, F<sub>4</sub>.*— $\text{Cd(NH}_4)_4\text{Cl}_2$ .

Pass  $\text{H}_2\text{S}$  through the solution. A pure yellow precipitate indicates  $\text{Cd}$ .

*Filtrate, F<sub>3</sub>.*— $\text{Sb}$  and  $\text{Sn}$  as stannates, thio-stannates, &c.

Pass a few bubbles of  $\text{H}_2\text{S}$  through the alkaline solution to remove any traces of  $\text{Pb}$ . Filter if if necessary, neutralise the solution with  $\text{HCl}$ , and then add an equal volume of conc.  $\text{HCl}$  (1·16), and boil till free from  $\text{H}_2\text{S}$ .

I. Treat 5 cc. of the solution with an iron nail or some levigated iron for a minute or two at about 90°. Filter into a solution of  $\text{HgCl}_2$ . A white precipitate or turbidity indicates  $\text{Sn}$ .

II. Heat the remainder of the solution to boiling, and saturate with  $\text{H}_2\text{S}$ . Cool carefully under the tap. If no precipitate forms add 2 to 3 cc. of water, shake, and keep under the tap for a few minutes. A red precipitate or yellow turbidity denotes  $\text{Sb}$ .

(NOTE.—The colour of the precipitate varies from bright red to pale yellow, and depends on the amount of

Sb present. A trace of Sb, 1 mgrm. or less, gives only a faint yellow turbidity. With a concentration of HCl of 5/N as above, no Sn is precipitated by  $H_2S$  in the cold, even when large quantities are present).

In order to test the method the following analyses were carried out, and the results in every case proved to be entirely satisfactory.

	Hg	Cu	As	Pb	Bi	Cd	Sb	Sn
	Mgrms							
1.	200	20	100	2	20	20	20	—
2.	—	200	5	—	—	—	100	5
3.	20	—	100	—	—	—	10	—
4.	—	100	5	—	—	—	100	10
5.	—	—	—	1	50	—	—	—
6.	—	—	—	—	—	—	1	250
7.	100	—	2	—	—	—	—	—

NOTE.—In Analysis 3 the HgS was practically completely dissolved by NaOH, due to the presence of a large amount of  $As_2S_3$ , but on boiling with  $H_2O_2$  was completely re-precipitated.

In conclusion, I desire to thank Prof. J. Walker for the interest which he has taken in the above work, and for much useful advice.

Chemistry Department,  
University of Edinburgh.

## PREPARATION OF SILICON CHLORIDES.

(A REPLY TO DR. KIPPING).

By GEOFFREY MARTIN.

My attention has just been called to an attack by Dr. Kipping (CHEMICAL NEWS, 1915, March 26th, p. 135) on my method of preparing chlorides of silicon (*Trans. Chem. Soc.*, 1914, cv., 2836) by the use of the new commercial product 50 per cent ferrosilicon. Dr. Kipping points out that Warren (CHEMICAL NEWS, 1892, lvi., 113) had previously suggested the use of a pig-iron containing 15 per cent silicon. Warren's process is perfectly hopeless from a practical point of view on account of the enormous excess of iron, which consumes too much chlorine.

The method has only an academic interest, and as such was not mentioned. My paper, in fact, was intended to describe merely the cheapest practical method available at the present time. As I pointed out in my paper, there is only one substance technically available, and that is 50 per cent ferrosilicon, which only came on the market on the large scale after 1902, long after Warren's paper. In fact, by using 50 per cent ferrosilicon one can obtain silicon at about 18s. a lb., against 18s. a lb. for technical 100 per cent silicon (pre-war prices). I explained this at length in my paper as originally submitted to the Chemical Society, and pointed out that this enormous cheapening of cost was the essential improvement of the method. Most unfortunately, however, these details were cut out of my paper by the Society as too "commercial" for a scientific publication. The two other methods mentioned in my paper, viz., Oersted's process and Gattermann's process, were at the time of their publication the cheapest methods extant, and were practical methods.

My paper was intended to deal solely with practical methods, and I had no intention of making a complete historical summary of all the methods which have been used or suggested for preparing silicon chlorides. As a matter of fact the principle of making chlorides of silicon by passing chlorine over silicon (either free or dissolved in metals in the form of silicides—it makes no difference) is not new, but dates back to the time of Berzelius (see Berzelius, *Fahres. Ber.*, 1825, iv., 91), and the use of silicides of magnesium, aluminium, iron, and copper have been suggested for this purpose. I believe, however, that my paper contains the first published

description of the use of 50 per cent ferrosilicon for this purpose, and this is all I claimed.

Dr. Kipping, therefore, is reading into my paper pretensions which are not contained therein and which are not claimed by me.

The further progress of Dr. Kipping's series of "researches" on my researches (see *Trans. Chem. Soc.*, 1913, ciii., 119; 1914, cv., 2861, &c.) are awaited with interest by the writer.

## PHOTOSYNTHESIS IN ORGANIC CHEMISTRY.\*

INTRODUCTION AND GENERAL CONSIDERATIONS.

By E. PATERNO

### NOTE I.—Introduction.

THAT solar energy, light, and heat are necessary to life has been known from the most remote antiquity; in the writings and poems of every age we find abundance of certain indications. Our aim is not that of occupying ourselves with the action of light in organic evolution and life, but to examine only the action of the light on the phenomena that are attributed to chemical affinity, combinations, and decompositions.

Contact, solution, heat, electricity, light, and radioactive emanations are the agents which determine the transformations of inanimate matter.

They produce, together with enzymes, bacteria, and the various high and low organisms, vegetable and animal, all the material evolutions of nature, with alternate vicissitudes, and with a motion that seems never to be at rest.

Now, among the various agents that determine and modify chemical activity in inanimate bodies, light is perhaps that which has received the least extensive applications, if we except the vast field of photography. The various solvents, heat, electricity, are used every day and every minute in laboratories and in factories. Who has recourse to the action of light? A cause of this is perhaps to be found in the fact that many reactions that take place from the action of light do the same, and more rapidly, on heating, and in the belief that resemblance of the action of light and heat is also greater than it is in reality. Berthollet, on the one side, and Gay-Lussac and Thénard on the other, in the beginning of the last century, tried to prove the unity of the chemical action of heat and light, and though Davy, in his "Elementi di Chimica agraria" (i., 45, Italian translation) stated that light has an action independent of that of the heat which it produces, he could not find a purely chemical example of it, but had to choose, in confirmation of his statement, one where the action of light is connected with a biological fact.

The earliest studies on the chemical action of light deal with the colouring of the salts of silver and with the bleaching of vegetable colours, although in the year 1725 Bestuscheff had observed the reduction of an ethereal solution of ferric chloride kept in the light.

On the alteration of silver salts in the light the first observation seems to be due to Schultze, in the year 1727, but the most important studies on the action of light on silver chloride (luna cornea) on the bleaching of colours under the action of light, and on the property of some bodies of becoming phosphorescent in the darkness, after being exposed to the light, were published by Bartolomeo Beccari, of Bologna, from 1731 to 1757. (I owe these notices on Beccari to my friend Prof. Guareschi, who is searching with so much love the part played by our fathers in the development of chemistry).

The argument was afterwards studied by Scheele, who in his famous "Traité de l'Air et du feu" (French translation by Baron de Dietrich, p. 129) occupies himself with light, and shows that solar light, concentrated at the focus of a concave mirror, decomposes the terre d'argent

\* From the *Gazzetta Chimica Italiana*, 1909-1914.

(carbonate), the chaux de mercuric (oxide), that solar light decomposes nitric acid, alters the luna cornea, reduces gold chloride, and above all he observed that the different parts of the spectra do not act equally, and the action is produced sooner with violet light than with the other rays. (On p. 264 of said work there is a note, evidently by the translator, where it is said :—This observation is common to Becari (*sic*), Meyer, Schultze, and Sennebier).

Important researches about the chemical action of light, independently of that which concerns the vital process of the plants, and that passes the limits of our examination, were afterwards made by the celebrated Count Rumford ("Philosophical Papers," i.), who studied the reduction of the salts of gold and of silver under the action of solar light, and that of a candle, imbibing their solutions with white silk, linen cloth, and cotton, and white magnesia; he also studied the behaviour of the solution of the salts of gold and of silver in presence of charcoal, turpentine, and olive oil. (Who likes to know more about this matter may see "Ueber die Chemischen und Physiologischen Wirkungen des Lichtes," von A. Kandurche, Marburg, 1834).

Wollaston (*Gilbert's Ann.*, 1811, xxxix., 291) and Herschel (*Phil. Mag.*, 1843) studied the action of light on the vegetable colours, and especially on the resin of guaiacum, which was afterwards utilised so well by Bunsen and Roscoe in their classical researches.

Of the argument Berthollet occupied himself with interest in his "Essai de Statique Chimique" (Paris, 1803), where Chap. III. (vol. i., p. 189) is devoted to the study of the action of light and of the electric fluid, and where it merits to be remarked that, dealing with the above mentioned experiences of Rumford, he says that the reduction of the oxides is owed to the carbon and to the hydrogen of the ether and of the oils.

Gay-Lussac and Thénard in the vol. ii. of their "Recherches Physico-chimique" (Paris, 1811) occupied themselves extensively with the manner of acting of light in the chemical phenomena (vol. ii., p. 186) with the aim of retrenching the last doubts as to the identity of the action of light and heat.

Important observations are owed to them on the alteration of the vegetable colours as saffron-red, logwood extract, Brazil-red, curcuma yellow, and wool and silk differently dyed. Having observed that light produces the same result as heat, and encouraged by the fact that violet rays, while they heat the bulb of a thermometer less than red rays, have a stronger chemical action, they conclude that light has very singular properties, and that the effects it produces cannot be reconciled with those of its different rays (p. 205).

To confirm the interest that the learned men of those times put in the study of light, I will say that in the "Philosophie Chimique" by Fourcroy (Paris, III.) in the first page he reduces all the facts and all the experiences of chemistry to twelve general phenomena, and first among these he puts the action of light.

But, from the application, made by Daguerre to photography, of the action of light on silver salts, the study of photochemistry grows so intermingled with the extraordinary progress of its application, that it is difficult from this mixture and from this thick net to sever the photochemical reactions from the purely chemical point of view.

We shall try our best to gather the principal facts that concern the action of light on organic substances, to which we shall restrict ourselves. From this limited point of view we can say that two facts were affirmed from the beginning of last century, namely, that light destroys the vegetable colours which it concurs to form in the living plants; on the other hand, that some substances, such as ether, turpentine, oil, exert a reducing action on some salts, and therefore give up to them part of their hydrogen.

Attempts have been made to group and classify the various reactions which light gives. And thus Ed.

Becquerel in an important paper (*Ann. Chim. Phys.*, 1843, [3], ix., 257) classifies the chemical actions of light in three groups, namely, bodies that undergo some physical change without change of composition, bodies whose elements are combined under the influence of solar rays, and bodies or combinations which are destroyed in part or totally by the influence of light; but in the examples that he conveys there is uncertainty, and so in the second series the phenomena of simple addition are confused with the more complex ones of the action of the halogens on hydrocarbons, and with phenomena of oxidation.

More recently a classification has been made by Roloff (*Zeit. Phys. Chem.*, xxvi., 337), and in this year H. Stobbe in a notable lecture given at the meeting of the Bunsen Society in Vienna (*Zeit. El. Chem.*, 1908, No. 33) has very cleverly distinguished between the various phenomena and different transformations that solar light produces in the compounds of carbon.

But to arrange all the photochemical phenomena with exact scientific judgment does not seem to me for the moment possible; among other things, the part that concerns the catalytic action that many attribute to light is still uncertain. It has long been known that the catalysing agents can determine combination in substitution of heat, and I have proved that porous carbon could substitute the insulation in the formation of carbon oxychloride (*Gazz. Chim. Ital.*, 1878, p. 238), a method which has been extended by Francesconi and Bresciani to the preparation of nitrosyl chloride (*Gazz. Chim. Ital.*, 1904, i., 13). But the very fact that heat, light, and catalysis can produce the same reactions and transformations, makes an exact classification of the transformations produced by only one of such agents a difficult task.

So Roloff, who, indeed, has never completed his publication, divides the action of light into physical and chemical, and includes among the former the stereochemical transformations and the polymerisations. According to us, on the contrary, these are true and far-reaching chemical transformations.

Stobbe makes a first division of the photochemical reactions of organic substances into reversible and non-reversible ones; but not even this distinction can be taken as a secure foundation of classification, because then the polymerisation of anthracene should be distinguished from that of vinyl bromide; while the condition of reversibility, or not, ought to be considered as a secondary thing, the principal and comprehensive phenomena being the polymerisation.

For my part I should be inclined to distinguish :—

1. The transformations, complete or partial, of a single substance into another single substance; under this heading are grouped the isomerisations, stereoisomerisations, polymerisations, the phenomena of phototropy, and intramolecular oxidations.

In this class the various reactions can be further distinguished as reversible and not reversible.

2. The decompositions and hydrolyses.
3. The reactions which take place between two or more substances, and which comprise the additions, the substitutions, the reductions, the oxidations, etherifications, &c.
4. The synthetical processes.

In the first group, as far as polymerisations are concerned, we may quote four different cases which represent the types of as many reactions; bromoacetylene, vinyl bromide, chloral, and anthracene. In the first case under the action of light takes place a polymerisation and tribromobenzene is formed, which, rather than a true polymeride of the first, is a new compound; in the second case the vinyl bromide is transformed into a polymeride, evidently of a very complex nature, but neither of these compounds in whatever way treated will regenerate the first compound any more; in the case of chloral we have the formation of metachloral or insoluble chloral, which regenerates the first product not in the dark, but by heating

at 100°; in the fourth case paranthracene is formed, which by sublimation, but also when taken away from the action of light, regenerates anthracene, a phenomenon so carefully studied by Luther and Weigert (*Zeit. Phys. Chem.*, li., 327).

These are evidently four types of different transformations, to which all the instances of polymerisation may be brought back.

For the transformation of the organic compounds in isomerides, it is enough to distinguish between the two cases of constitutional isomerism and stereoisomerism; an example of the first case we have in the transformation of angelic into tiglic acid observed by Wislicenus, while some examples of the second case are the transformation of cinnamic into allocinnamic acid (Liebermann, *Ber.*, xxiii., 2510; xxviii., 1443), of maleic into fumaric acid (Sachs, *Ber.*, 1895, p. 489), of some oxymes into the syn form (Ciamician and Silber, *Gazz. Chim. Ital.*, 1904, ii., 129).

With some cases of phototropy, a name introduced by Marckwald (*Zeit. Phys. Chem.*, 1899, xxx., 140) to whom are due the first observations of it, and the statement that they are all reversible, Stobbe dealt with success in his important studies on fulgides (*Annalen*, ccxli., 333), and Prof. Piutti, who has described a series of phototropic compounds, among which we shall mention some imides of phthalic, pyrocinnonic, and maleic derivatives, fumaric and metaconic diamides, and some phenylic derivatives of itaconic acid (*Gazz. Chim. Ital.*, 1903, 1906, 1907, 1908).

And still in the first class of transformation of a single substance into another, the intramolecular oxidations are worthy of particular attention. They have been observed in the nitric compounds, and examples, not however due to the action of light, had been observed by Baeyer in the formation of indigo from *o*-nitrophenyloxyacrylic acid (*Ber.*, xiii., 2262), and *o* nitrophenyllactimethylketone (*Ber.*, xv., 2856), in the formation of isatin from *o*-nitrophenylpropionic acid (*Ber.*, xiii., 2259).

A characteristic transformation is that, observed as early as 1895 by Friedländer, of the nitronaphthalindisulphonic acid in nitrosonaphtholdisulphonic acid (*Ber.*, xxviii., 1535). A quite similar reaction takes place under the action of light, and Ciamician and Silber have proved that nitrobenzoic aldehyde is transformed into nitrosobenzoic acid, *o*-nitropiperonal into *o*-nitrosopiperonillic acid.

In the second group we have included the decompositions and the hydrolyses provoked by light. For the decompositions, in the strict sense of the word, there are but few examples in mineral chemistry, and I think it is difficult to find any among the organic compounds. The alterations undergone, *e.g.*, by the alcoholic iodides, besides not having been yet thoroughly studied, cannot be simple molecular splitting into more simple parts, and generally all the instances commonly quoted as decompositions of organic substances by light are real transformations, which come in again into the other cases.

Perhaps a case of decomposition which may be taken as an example is that of nickel carbonyl which is rapidly decomposed in the light (Dewar and Jones, *Proc. Roy. Soc.*, 1907, lxxix., 66). As to examples of hydrolysis, it is enough to mention the researches of St. Victor and Corvisart on starch (*Annalen der Chemie*, cxlii., 112), and that of cane-sugar observed by Raoult, and the others observed by Ciamician and Silber on the ketones (*Ber.*, xxxiii., 1583, and *Lieben's Jubelband*, 1906), where it is proved that acetone splits into acetic acid and methane, methylethylketone into acetic acid and ethane, while menthone, a cyclical compound, by the opening of the ring furnishes decylic acid.

The reaction is the same as that observed by Chancel in 1860 with benzophenone, which splits into benzoic acid and benzene, and is completed by that studied by Fay (*Am. Chem. Journ.*, 1896, and *Annalen*, ccxxii., 262), who has proved that acetic, propionic, and isobutyric acids, in the presence of uranyl salts and under the action of light, give methane, ethane, and propane.

The third group comprehends the additions, substitutions, etherifications, and the processes of oxidation and reduction. The phenomena of addition in the organic compounds, especially with halogens, are numerous enough, and many are facilitated by intervention of light, others do not come except with the light; it is not worth while to mention examples because they are too obvious. It is enough to remember that according to Wislicenus (*Annalen*, cclxxii., 98) tiglic acid adds bromine only in the light, while its isomer angelic acid adds it only in the dark. Also the phenomena of substitution of the halogens in organic compounds are facilitated by light, and generally the higher substituted products are not formed without its intervention. It is enough to remember the works of Dumas, of Malaguti, and of Regnault to find numerous examples of what I say. But an important fact is known as to the formation of the products of substitution, namely, their difference, according as the preparation is made in darkness or in light. It was already known that heat produces the same effect, and we must remember the action of chlorine and bromine on toluene, which at low temperatures enter in prevalence into the aromatic nucleus (Beilstein and Geitner, *Annalen*, cxxxix., 132), while at high temperatures they enter chiefly in the side-chain. The same happens and more decidedly with light; so Schramm has found that, among the homologues of benzene, in the light the halogens enter in the side-chain, and without it they enter in the nucleus (*Ber.*, xviii., 350, 606, 1272; xxix., 212). H. Apolski has also studied the chlorination and bromination of thiophene (*Phys. Centr.*, 1906, iii.).

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, March 25, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"The Production of Growths or Deposits in Meta-stable Inorganic Hydrosols." By Prof. B. MOORE, F.R.S.

"On Forms of Growth resembling Living Organisms and their Products slowly deposited from Meta-stable Solutions of Inorganic Colloids." By Prof. B. MOORE, F.R.S., and W. G. EVANS.

"A Contribution to our Knowledge of the Chemistry of Coat-colour in Animals and of Dominant and Recessive Whiteness." By H. ONSLOW.

This research was undertaken in order to discover a chemical method of differentiating the two similar forms of white animals known as Dominant whites and Recessive whites, or albinos. Hitherto this has only been possible by observing their genetic behaviour.

Dark animal pigments are believed to result from the oxidation of a colourless chromogen by an oxydase. The skins of young black rabbits were found to yield a tyrosinase which converted tyrosine to a melanin. By means of this tyrosinase it was possible to test extracts from white rabbits of both types.

Briefly, extracts from Dominant whites contained an anti-oxydase which inhibited the tyrosinase of the black rabbit extracts. Extracts from albinos, on the other hand, had no inhibiting influence, and were themselves incapable of producing any pigment. The anti-oxydase was also found in those white parts of rabbits which are Dominant to colour, such as the white bellies of the wild rabbit and of the yellow rabbit carrying agouti.

These results tend to confirm the Mendelian view that Dominant whiteness is caused by a factor which inhibits the pigment-producing mechanism if present, and that

albinism results from the partial or total absence of the factors necessary for the development of pigment.

The experiments also revealed facts which suggest that the difference between pigments producing black, chocolate, and yellow hairs is quantitative rather than qualitative, for after extraction the pigments in all three colours appear identical.

That variation in colour is a structural modification is supported by the fact that dilute colours, such as blue, are caused by a lack of pigment in the cortex. In the corresponding intense colours, such as black, pigment being present in the cortex, the white light reflected from the vacuoles is absorbed, thus deepening the colour.

#### INSTITUTION OF CHEMICAL TECHNOLOGISTS. (LONDON SECTION).

Colonel CHARLES E. CASSAL, V.D., President of the Institution, in the Chair.

(Continued from p. 203).

IN an able lecture delivered before the British Association in 1901, Professor Green stated that the remedy for the existing condition of affairs in connection with British chemical industry could only be found in the better appreciation of the value of science throughout the length and breadth of the land, and that it is not so much the education of our chemists which is at fault as the scientific education of the public as a whole. The ignorance of the general public in regard to science and the value of science is accurately reflected in our legislature, representing as the latter does in the mass the greatest stupidity of the greater number, and is indicated by the ignorance and ineptitude of the State in dealing with science and with scientific problems. It is only by meetings such as this and by their constant repetition that this fundamental point can be impressed upon the public and their representatives.

Sir William Perkin in an address to the Chemical Society in 1885 stated that the success of the German chemical industries was due to the employment of high-class professional chemists. The truth of this is so obvious that it ought to be unnecessary to put forward the statement. What steps, however, do the majority of our manufacturers take to encourage the high-class chemist, and what steps do the Government authorities take in the same direction? In an advertisement recently issued by the Inspection Department of the Royal Arsenal, Woolwich, the value placed by Government departments on scientific services *even at the present time* is clearly indicated. I will quote the advertisement:—

"Inspection Department, Royal Arsenal, Woolwich.

"Wanted immediately, Temporary Assistant Chemists. Applicants must have had a thorough training in Inorganic and Organic Chemistry, and must be accurate Analysts. University graduates or members of the Institute of Chemistry will have preference. Wages £2 *es. 6d.* per week.

"Applications, giving particulars of training and experience and accompanied by copies of not more than three recent testimonials, should be addressed to Chief Inspector, Royal Arsenal, Woolwich."

If a Government department sets such a scandalous example what is to be expected from the ordinary manufacturer?

Referring to this in a letter to the *Daily Chronicle*, Sir William Tilden observes:—"Does Chief Inspector seriously think that a trained chemist is worth no more than the 'wages' he offers, which are subject to the deduction of 4*d.* a week for insurance? Does he realise that the kind of man he is asking for has in all cases spent at least five or six years in acquiring his technical skill and during that time has provided maintenance and fees at his own cost? I am informed that these assistant chemists

have been wanted for the last three or four weeks, but that no applicants for the posts have appeared—hence the advertisement. If any applicants do turn up it is certain that like all other scientific men of British birth they are animated by the patriotic desire to be useful to their country, and are willing to disregard official insolence. But it will have to be remembered that when the war is over the Government of this country will not continue to receive scientific assistance at the 'wages' of the unskilled labourer, alongside of whose labour it is now ranked."

In an advertisement which recently appeared in the *CHEMICAL NEWS*, a "highly-trained chemist," who had to be a "University Honours man," was sought, and the "salary" offered was £65 a year. Similar examples might easily be multiplied. I will give another that has just been brought to my notice and which indicates the sort of treatment that the scientific chemist is expected to submit to. This example relates to a form of agreement between the chemist and his employer in regard to an appointment to be made by an English firm at, of course, a miserable rate of remuneration.

"If during the continuance of this Agreement the employee shall discover, invent, or otherwise become possessed of any process or improvement in the manufacture of or otherwise relating to — he shall forthwith communicate the same to the Company, who shall be at liberty to apply for Letters Patent in all countries for the same in their own or any other name or names, and all such Letters Patent, when obtained, shall be the property of the Company, and the Company shall pay all fees in connection with such patent.

"If the Company is unable to apply for and obtain any Letters Patent in any particular country for any such inventions and improvements in its own name the employee shall, at the expense and request of the Company, apply for and obtain such Letters Patent in his own name, and the same shall when obtained be forthwith assigned to the Company for a nominal consideration of ten shillings, but at the expense of the Company in all respects."

Can any more striking example of how *not* to do things be afforded than the ridiculous exhibition which the Government has made of itself in regard to the Dye Industry? To control the operations of "British Dyes, Limited," a Board of Directors has been appointed, on which I believe I am right in saying that there is not only not a single representative of the branch of chemical science specially involved, but not even a single scientific chemist. There are two chairmen of railway companies and a chartered accountant, but no man skilled in chemistry to assist in the control of a national chemical industry. It would appear, however, that a Committee consisting of scientific experts is to be appointed "to assist the Board on technical points." In other words, a Committee of experts is to be kept in a back room to be consulted when the non-experts who compose the Board see fit, in their wisdom, to do so, but this Committee is, of course, to have no power of control or any voice in the management of the concern. Can anything more absurd be imagined, or anything more derogatory to the men of science who are to be so contemptuously treated?

It is not clear whether "British Dyes, Limited," are going to manufacture and sell such drugs as are by-products in the manufacture of dyes. This matter, as one newspaper expresses it, has been left in a "conveniently nebulous" condition. Unless these drugs are manufactured "British Dyes, Limited," will not be able to produce the dyes at a reasonable commercial price. It is absolutely impossible to carry out this branch of the industry, at any rate without the continuous co-operation of the most highly-trained scientific chemists and ample provision for research.

It is absurd to suppose that a Board of so-called business men will be capable of managing this business successfully, in view of the fact that the matters to be dealt with involve intimate and thorough knowledge not of one highly specialised branch of science only, but of several.



The subject is one of the utmost complexity, and if success is to be attained it must be approached and dealt with in an entirely different manner. The first essential is a properly-constituted Board of Directors adequately representative of the chemical profession, of the trades concerned, and of finance. The very best technical and business advice is absolutely necessary. A Board composed merely of business men, however able they may be, is not in a position even to understand the problems they will be called upon to solve. As Prof. Meldola has recently pointed out, the position of the business men in question will be precisely similar to the position of a man who imagines that because he can tell the time by looking at his watch he is competent to undertake the management of a chronometer factory. Unless the Board is entirely reconstituted the opportunity of establishing a great dye industry in this country will be lost for ever.

To ask the public to subscribe £1,000,000 for the purpose of running a concern which is to be mismanaged in the manner indicated is hopelessly ridiculous. Moreover, in view of the persistent refusal of the Government effectively to protect British Dyes, Limited, against German "dumping" after the war, who but a fool would put his money into a concern which, for this reason alone, is doomed to utter failure?

In the limited time at my disposal I cannot hope to do more than to open the discussion in a general way, and I do not wish to stand between the meeting and those who are more capable of dealing with the subject before us than I am. The questions involved are far too vast to admit of their being adequately dealt with in the course of an introductory speech, or on a single occasion, by an individual or by one meeting. In conclusion, I shall merely allude to the unscrupulous, and in fact grossly dishonest, German competition to which British chemical industry has been subjected, and to some few of the steps which in my view should be taken to prevent that competition in the future. At a recent meeting at the Society of Arts Sir William Ramsay pointed out that in trade as in war the Germans are untrustworthy, unscrupulous, and cruel, and in an article published in *Nature* in November last he summed up the course of action adopted by the Germans in the following words:—

"First, in the organisation of a German chemical business, the management consists not in a board of well meaning elderly gentlemen with a works-manager in their employment, but in a board of specialists, whose business in life is to manage the factory financially, chemically, and as engineers, and who are very highly paid for their services. Second, these gentlemen and a special staff are continuously on the look-out for any scientific discovery or invention which can prove of advantage to their business. Third, a very large staff of men, trained in universities or technical schools, is turned on to the problem of making such a discovery commercial, whether by securing cheap raw material, cheapening the process of manufacture, or creating a public demand for the article to be manufactured. Fourth, a legal staff is maintained, whose business it is to protect by patent all improvements, however apparently trivial, and to describe them so vaguely as to conceal them from their competitors; these gentlemen in some cases have also to advise whether piracy is likely to be successful: whether it may not be possible by infringing a patent so to saddle an opponent with legal expenses as to break his competition. Fifth, such companies are so powerful that they can influence the central Government to protect all new developments, whether by imposing duties on articles which might possibly compete, by extending bounties to exported products, or by securing advantages in freights to the coast and in shipping the goods abroad. Sixth, agencies are maintained all over the world whereby the article is introduced to the notice of foreign purchasers, and last, an extensive credit system is encouraged."

At the Society of Arts meeting Sir William Ramsay went on to say:—

"German competition is thoroughly organised and systematic; their plan has been to attack some material manufactured here, and, by one of the means alluded to, to render its manufacture unprofitable. Having obtained a monopoly, prices are raised. That is a not unusual method of commercial warfare, but it is only in Germany that all the resources of the State combine to render it easy. How are such tactics to be met? First of all, there must be co-operation and trust among our chemical manufacturers. They have to be taught to fight, not each for his own hand, but against a common enemy. Smaller works, which have not funds to maintain an expensive research staff, must combine to obtain efficient laboratories; the products of one works must supplement those of another, and the manufacturers must be organised. Second, competition which is unfavourable, owing to fiscal regulations or patent laws, must be combated by the action of the State, after advice and careful consideration, so that our manufactures and trades may not be unfairly attacked by duties, by export bounties, or by easy freights. We are now fighting for our life, and, as has happened during the present crisis, politics must go to the wall under the pressure of events. All parties in the State should and must work together for the common good. Unless that is our spirit, ruin will inevitably and deservedly overtake us."

In a recent article by Mr. Wilberforce Green (*Journ. Chem. Tech.*, ii., 54) it is pointed out that—"It seems to have become a fixed belief with a certain type of British manufacturer that it is best to employ a German chemist, or to retain the services of a German technical adviser. In the mere trader's eyes such a man has the paramount virtue of usually being 'cheap', but things are very rarely obtained for less than they are worth, and the German chemist is often dear at the price. The myth of the German 'superman' has been completely exploded during the last few months, and the much-vaunted Teuton has appeared before the world in his real character. He is not, as has been so foolishly believed by many of our countrymen, the intellectual, moral, or physical superior of the despised Englishman. He is very far from being the equal of the latter, nor is he in any way technically sounder. His employment in British concerns commends itself neither to patriotism nor to common sense. With the mere huckster, however, cheapness is more than patriotism, and common sense is blinded by illusive visions of profit. So far as English technical chemistry is concerned, the explanation of the presence of Germans in controlling positions is directly due to the want of professional co-operation in the chemical profession. English chemists have not enforced the recognition of the value of their work to the community; they have not attempted to put their profession on the same footing as the other learned professions; they have not made it understood—in fact they do not themselves appear to have appreciated—that in manufacturing industries everything is based on science, and that whoever is in a position to control the practical applications of that science is he who is really controlling the industry. If we are to advance the scientific chemist must take his proper place. As Sir William Tilden has recently said, 'The operations in which materials are to be employed in producing and controlling chemical reactions which lead to the chemical product belong to the chemist, and here he ought to be supreme.' Unless the English chemist takes his own part he will continue to be undercut by the foreigner. Once the chemical profession is organised on a rational and national basis, however, the alien interloper could be automatically excluded. Without proper organisation that most desirable end will never be attained. At present we find Germans exercising an extensive and dangerous influence in the management of bodies that claim to govern professional affairs and professional conduct, or who are mixed up with the interests of British industrial chemistry. We say emphatically that, excepting in a very few special cases, all Germans, whether naturalised or not, should be expelled from those professional or semi-professional socie-

ties. These people are the fellow-countrymen of those who are responsible for the bestial excesses that have characterised the influx of the German hordes into Belgium and France. Unless the contrary be known and proved, they must be presumed to be intellectually and morally on the same level as the 'cultured' professors who have so warmly expressed their natural admiration for murder, rape, robbery, and incendiarism. We cannot conceive how any self-respecting bodies of men can now continue to tolerate the company of the many Germans who at the best can only be regarded as suspects, and who form a not inconsiderable proportion of their membership. Still less can we understand the reception of such people on terms of equality by granting them membership or fellowship. It may be said that some of them are 'naturalised,' or have lived in the country for a long time. This is, in fact, the plea often put forward by Germans arraigned on criminal charges at our police-courts. But it is very plain that naturalisation means nothing to a typical German. It is on all fours with a charm written on 'a scrap of paper.' Naturalisation does not necessarily convert a typical Hun into a decent person, or make him a trustworthy member of society. A man may have a *peuchant* for keeping skunks as pets, but a verbal or written statement from him that the skunk is a pleasant and well-mannered beast would not inspire a second party with confidence if the first-named proposed to introduce skunks into his drawing-room, for the skunk would behave as its nature prompted it.

"Many of the societies and associations are presumably concerned directly or indirectly with the development and progress of British technical chemistry, and yet they have on their registers names which indicate that their possessors have had the priceless advantages of Teutonic origin and 'culture.' Such men are not interested in the development of British commercial enterprises apart from purely personal success; still less are they concerned with the building up of the British chemical profession. A profession demands a high standard of conduct, both individual and corporate, and to suppose that the countrymen of the moral abortions whose acts have disgusted the civilised world have necessarily changed their nature with their country is absurd. These outcasts in our midst are largely responsible for the lack of co-operation in the chemical profession. True professional unity is impossible under such conditions.

"It is not merely a question of scientific ability and technical skill. Many an expert thief is a good craftsman, but one would not knowingly employ such a person to carry out repairs in one's house. Something more is demanded of men than mere skill in material matters. It is the ethical outlook that really counts in the long run. If we find a profession harbouring and countenancing persons who, by race, temperament, and education are unfitted to occupy any positions of trust, then the position of that profession is obviously imperilled.

"After the welfare of his country a man regards his profession as of the next importance. He thinks so presumably because his education enables him to appreciate the close relation that exists between the right conduct and development of his profession and national honour and security. We are all trustees for the future, but it seems that professional men have a heavier share of responsibility in this respect than others. They cannot regard their profession as detached from and independent of national needs and aspirations, but an alien of the character described can have no higher views of the profession into which he has contrived to enter than as a means of enabling him to turn the products of his brains into cash as expeditiously and extensively as possible."

As President of this Institution and as a professional chemist with an experience extending over nearly forty years, I thoroughly agree with and endorse the statements which I have quoted. I go even further, and I say that now and after the war it should be made a criminal offence to give employment of any kind to a German in this

country. We have been told to think scientifically by a gentleman whose spiritual home is in Germany—whose physical home should, in my opinion also be there—and who has demonstrated his own apparently hopeless incapacity to do the scientific thinking which he recommends. Despite the source of the advice, let us endeavour to think scientifically, and to act scientifically in regard to this great question, and I appeal to my professional brethren and to the public at large to support the Institution in the campaign which it has initiated. (Cheers.)

Mr. WILLIAM THOMSON, F.I.C., F.R.S.E., Vice-President (Director of the Royal Institution Laboratory, Manchester).—Mr. President and Gentlemen, this subject—how the British dye industry is to be carried on after the war—is one which will require very careful consideration as to what the British Government will do in the future. It is perhaps impossible to say what is the best method of procedure, but I think one thing we can say is that the method the Government have thought best to adopt is not the right one. Business men believe that they need some guarantee from the Government that they will not lose the money they expend through unfair German competition after the war. There are various methods of dealing with the matter. One is to give protection. That opens a very big political question as to how far you can protect the dye industry and not protect a great many more industries. This method will therefore probably fail. There is another means which may be considered, and that is to adopt some modification of the principle which the Germans themselves have already adopted. The policy of force, the policy advocated by their favourite philosophers, Nietzsche, Treitschke, and Bernhardt. Why should the Allies not treat Germany as she has treated Belgium? Compel her to pay an indemnity of, say, eleven thousand millions of money during a number of years and take her industries from her and use them against her for our own benefit till the indemnity is liquidated; that is what she would do with our industries if she had the chance.

Mr. C. R. DARLING, A.R.C.S.I., F.I.C. (Finsbury Technical College).—Mr. President, the remarks I might make would only be from an educational standpoint—that is, to give my impression how our educational system is likely to work. It seems to me that we have made, in the past, too great a distinction between "pure" chemistry and applied chemistry, which we ought to call, I suppose, "impure." A number of those who have devoted themselves to pure chemistry look on industrial chemistry as beneath them. I think that is one of the reasons why we lag behind in our chemical industry. It is not realised that research for industrial purposes ought to get the same scientific recognition as pure theory. We have to get rid of intellectual snobbishness, and to regard research of any description as being equally vital. That, I think, is one reason why we have failed to keep pace with Germany in this respect. I cannot say that I associate myself with the policy advocated from the platform. I have been one of those who hold that science ought to have no national boundaries. I do not think we are going to gain by copying the brutality of our opponents. Let us march ahead and do whatever we do in a gentlemanly way, for that is the best procedure. There is one other aspect of this question and that is this:—the teaching of our colleges; how far does it go in providing manufacturing chemists with the men they require? My own experience is that the methods of colleges in general require a good deal of amendment. The courses are, in the main, of a theoretical nature and are devoted to the obtaining of a degree. The student does not care what he learns so long as he gets a degree, and the examinations for these degrees are conducted on theoretical lines. The result is that all the teaching of the colleges has a theoretical bias and the student is of little or no use to the technologist. It would be difficult for us—indeed not possible—to make a man a trained technologist. I submit our educational institutions could cause several improvements to be made

to make a man at least useful as a technologist. There is another improvement to be effected and which must come from the manufacturing side. I do not think there is a more distressing sight than the average works chemist in this country. (Hear, hear.) My professional duty takes me to many establishments and I have been ashamed at the way the works chemists are treated. They are, many of them, kept in a corner and any improvements they want to make are stifled at once because it entails expenditure. The directors never object to buying a new engine; they never seem to object to the expenditure of £1000, but if the works chemist suggests £20 the directors refuse to pass it. I have been disgusted with the stupidity of those in charge. I do not know how other establishments are conducted, but I know that in some cases failure is due to the fact that instead of appointing the scientific side to control the business a lot of lucrative positions are held by the sons of directors who know very little about chemistry. If we are to compete in future with Germany what we have to do is to commence by first of all educating the manufacturers as to the value of chemical knowledge and research, and to give them proper students from the colleges, and then for them to treat those students properly and to give them a chance. And I do not see why, in the future, our chemical industry should not then hold its own. (Cheers.)

(To be continued)

## NOTICES OF BOOKS.

*Molecular Association.* By W. E. S. TURNER, D.Sc. (London), M.Sc. (Birmingham). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THE account given in this book of the experimental data relating to molecular association which have been accumulated and the theoretical explanations advanced is particularly clearly worded, and the book is an important addition to the literature of physical chemistry. The methods which have been employed in the study of the subject are excellently described, and the phenomena of the molecular complexity of dissolved substances are fully treated. A short general review of complexity in the liquid state contains an unprejudiced criticism of the methods which have been used in investigating this subject and the deductions made from the results obtained. The molecular complexity of water and the theory of dynamic allotropy are very fully treated, as well as the effects of association on physical properties. A lengthy appendix, which alone would make the monograph of great and permanent value for reference, gives the results of all experimental work on the molecular complexity of dissolved substances.

*A Manual of Oils, Resins, and Paints.* By HARRY INGLE, D.Sc., Ph.D., F.I.C. Volume I., "Analysis and Valuation." London: Charles Griffin and Co., Ltd. 1915.

THE opening chapter of this book gives a much condensed account of the chemistry of the oils the utility of which must be regarded as somewhat doubtful. The later and more practical parts of the book will, however, be found quite sufficient for their purpose, that of providing the analytical chemist with reliable information relating to the analysis of oils, chiefly for technical purposes. Methods of applying physical and chemical tests are briefly but clearly described, and concise accounts are given of the systematic examination of oils, fats, and waxes, and their estimation in such substances as seeds, oil cakes, &c. The technological examination of various products, e.g., varnishes, paints, soaps, linoleum, &c., is treated fairly fully, and many useful tables of oil constants are given.

*Dye-stuffs and Coal-tar Products.* By THOMAS BEACALL, B.A. (Cambridge), F. CHALLENGER, Ph.D., B.Sc., GEOFFREY MARTIN, Ph.D., M.Sc., B.Sc., and HENRY J. S. SAND, D.Sc., Ph.D. London: Crosby Lockwood and Son. 1915.

THIS book is a reprint with some additions of parts of Volume I. of "Industrial and Manufacturing Chemistry," and deals with the manufacture of dyes, inks, sweetening products, drugs, and photographic chemicals. It appears at an opportune time, and students and chemists will welcome an English book on these substances, the manufacture of which is engaging so much of the attention of the scientific and commercial world. Although the book gives only summaries of methods of preparation and cannot be regarded as an exhaustive treatise it will be found useful by reason of the full references it gives to patent and other literature, and every endeavour has been made to make the treatment as practical and the information as accurate and up-to-date as possible. Statistics relating to imports into the United Kingdom and the United States of the dyes, drugs, &c., are included.

*Oedema and Nephritis.* By MARTIN H. FISCHER. Second and Enlarged Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1915.

THERE is in this book necessarily a good deal of matter which deals with debateable views, and some of the author's conclusions are at variance with those of some of the most eminent authorities. He displays no reluctance to state his opinions with great definiteness, and shows himself an adept in putting forward his arguments in the most cogent manner, which must be admired even by those who differ from him and who see much to criticise in his deductions. An admirable feature of the book is the abstract of the whole which serves as the introductory chapter. In this review is given, section by section, of the text, and it will be much appreciated by the busy reader. In the new edition the results of the latest experimental and clinical observations have been added, while the main argument remains unchanged.

## OBITUARY.

DR. W. J. SELL, F.R.S.

WILLIAM JAMES SELL, M.A., Sc.D., University Lecturer and Senior Demonstrator in Chemistry at the University of Cambridge, died at Cambridge after a long illness on March 7, 1915. He was born at Cambridge in 1847, and for more than fifty years was connected with the chemical laboratories there, and contributed in no small degree to their development and success. He was barely fifteen when, on the recommendation of the master of the elementary school which he attended, he was employed at the chemical laboratory of St. John's College, at that time the only one in the University open to undergraduates. Here he learnt elementary analysis and the use of apparatus, heard the professor's lectures, and saw his experiments. He made good use of his opportunities, and soon made himself an efficient assistant. In 1865, when the Jacksonian Professor of Natural Philosophy removed his apparatus into a new building, the room vacated by him was united with that of the Professor of Chemistry and a room built above them for a student's laboratory; the first step taken by the University, in its corporate capacity as distinct from the Colleges, to provide experimental training for its students. Here Sell was appointed attendant, and had charge of the apparatus, and not only assisted the professor in the experiments at his lectures, which at that time embraced physics as well as chemistry

proper, but was much in demand to help students whose notions of making experiments were often crude. The laboratory was a poor place at best in comparison with modern laboratories, but it grew and became filled with students, to which result Sell's help contributed not a little. In 1870 he married, and soon after entered Christ's College and matriculated in the University. He had acquired a good knowledge of chemistry and of some other branches of natural science, and knew a little of modern languages, but no degree could be obtained at Cambridge without some acquaintance with Latin and Greek, and he had not learnt either. It was a formidable task to begin now, but he faced it with his usual quiet determination, studying Latin and Greek at all times when his duties at the laboratory permitted, passed the examination in both languages, and was then able to take the Natural Sciences Tripos for his B.A. degree. In this he obtained a first-class honours, for chemistry, in 1876. This success brought him private pupils, and therewith an increased income, very necessary for him because University posts were all meagrely paid; at the same time he took a Demonstratorship instead of remaining assistant to the professor. A short time afterwards he succeeded to the place of Principal Demonstrator. Although his position in the University, thenceforward to the end of his life, was that of a Demonstrator, it must not be supposed that his public teaching was confined to what is usually known as demonstrating, which is mainly done by the junior members of the staff. On the contrary, inasmuch as chemical science was constantly expanding and learners increasing in number, the lectures had to be more specialised and the classes subdivided. The University had not the means to multiply the professors, and so the staff of the laboratory had to meet the demand for more instruction as best they could amongst themselves. In this Sell was most serviceable. He shirked nothing so that the teaching might, so far as lay in his power, keep pace with the growth of knowledge, and for many years was in reality an effective professor, though in name only demonstrator. He was never what is called a brilliant lecturer, but was a sound teacher, who gained the confidence of his hearers, and attracted them by his painstaking sincerity and willingness to help anyone in difficulty.

He had been elected a Fellow of the Royal Society of London in 1900, and took the degree of Sc.D. at Cambridge in 1906. A attempt was made to get him promoted to the rank of Reader in Chemistry. The University has full power to do that, and there were similar applications in connection with other branches of learning, and Sell's friends thought that his distinction as a chemist, and his long and faithful devotion to the service of the University, gave him a claim to promotion at that time before any other aspirant to the same rank. The appointment of readers, however, does not rest with the University at large, but with a Board composed of representatives of the various departments of knowledge, literary as well as scientific; in fact, with a body of specialists chosen as such. As always happens in such cases, every member of the Board thinks that his foremost duty is to see that his own particular subject of study gets its share of money and places, and magnifies it accordingly, so that the Board hardly ever pulls together for the general advantage, still less to do justice to an individual. No readership was created at that time, and all the recognition Sell got was his appointment to a University lectureship with a stipend of £50 a year.

In his younger days, when it was as much as he could do to maintain his family, he could hardly spare time for original investigations; but later, when the laboratory was grown up and needed less nursing, he was able to show that he had the capacity for successful research and the will to advance knowledge himself, quite as much as to put others in the way of doing it. He will be best known by his work on pyridine derivatives, to which he was led by previous studies of citrazinic acid. These were the subjects of a large number of communications to the

Chemical Society from 1892 onwards. In some of these researches he was assisted by one or other of the advanced students in the laboratory, while in other cases he worked alone. Without going into details it may be mentioned that from pyridine he obtained eight distinct chloro derivatives, and from pyridine hydrochloride, in addition, some remarkable dipyrindyl compounds. Moreover, he did not fail to demonstrate the chemical constitution of most of the new compounds he discovered. Other subjects of interest investigated by him were the salts of a base containing chromium and urea, and colloid solutions of phosphates. All he did bore the stamp of careful accuracy, and he impressed on his pupils the necessity for sparing no pains to ensure this, if any real advance of knowledge were to be made.

He was so unassuming that only those who had known him long found how much was hidden under that modest behaviour. It really meant that he wished always to do what was right, whether convenient or inconvenient, and to believe other people to be as good as himself.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx., No. 9, March 1, 1915.

**Catalytic Reduction of Indigo.**—André Brochet.—Indigo can readily be reduced by hydrogen in presence of active nickel. The indigo, either dry or in the form of a paste, is suspended in water containing a little caustic soda, and active nickel, kept away from contact with air by means of boiled water, is added. When this mixture is shaken in an atmosphere of hydrogen the indigo is converted into white indigo, which gives the usual yellowish green solution. The action takes place at the ordinary temperature, and becomes very rapid at 60° to 80°. It takes place in a neutral medium, although more slowly. The nickel retains its activity for a very long time.

No. 10, March 8, 1915.

**Catalysis in Oxidation of Alkaline Sulphites.**—Emile Saillard.—The author has made a study of catalysis in the sugar industry, especially with reference to alkaline sulphites, dissolved in the juice or sugar syrups. Some catalysts retard and others accelerate the oxidation of alkaline sulphites. It is observed that more sulphates are formed when juices containing 12 per cent of sugar are sulphited than from syrups containing 50 per cent of sugar. More sulphates are formed also when the temperature is raised. It is difficult to oxidise alkaline sulphites of molasses by bubbling air through them. In some sugar factories sulphitation is carried out with gases from sulphur and lime furnaces simultaneously. The sulphite and carbonate of calcium formed induce the transformation of sulphites into sulphates. In the same way if juices containing precipitable lime are sulphited the sulphite of calcium obtained in suspension may favour the oxidation of dissolved alkaline sulphites.

## MISCELLANEOUS.

**The Molecule of Carbon.**—F. V. Della-Croce.—The density of a gaseous compound is never lower than that of the constituent gases, since the volume is never greater than the sum of the volumes of the constituent gases, and is obtained by adding together the products of density of each gas by its volume, and dividing by 2. Thus the density of  $\text{NH}_3$  is  $\frac{0.694 \times 3 + 0.969}{2} = 0.5886$ . Considering the

case of CO, since the densities of the compound gas and of oxygen are known, we can obtain an equation for the density of carbon vapour; i.e.,  $\frac{x}{2} + \frac{1 \cdot 10523}{2} = 0 \cdot 9670$ ,

where  $x$  = density of carbon vapour. This gives  $x = 0 \cdot 8287$ , and the calculated and observed densities of other compounds of carbon agree very well when this value of the density of carbon vapour is employed. The molecular weight of carbon vapour would then be  $0 \cdot 8287 \times 28 \cdot 818$ , and this gives 2 for the atomicity of the carbon molecule. The atomic weight of an element having a diatomic molecule is the same as its density in the gaseous state, referred to that of hydrogen. The calculated atomic weight of carbon is then  $11 \cdot 92$ , which agrees very well with the value obtained by chemical methods.—*Moniteur Scientifique*, No. 878, February, 1915, p. 25.

The British Empire Industrial League.—It is a remarkable fact that in London, the greatest business City in the world, there exists no commercial club of national or imperial scope. The lack of such an institution in the metropolis is a great inconvenience to the manufacturers, merchants, shippers, and business men of the British Isles, and is, above all, keenly felt by commercial visitors from our colonies and foreign buyers visiting London for business purposes. The Council of the British Empire Industrial League have given serious consideration to this matter, and are making arrangements to found in London the British Empire Commercial Club, on such a basis as will supply metropolitan, national, and imperial requirements. Such a business club, properly conducted, should be a very great benefit to British industry, commerce, and trade, and the enterprise, as a matter of course, should receive the hearty and generous support of our manufacturers, exporters, and wholesale and retail merchants—in fact, of all our leading men connected with business. The Lord Mayor of London (Sir Charles Johnston) and the Lord Mayor of Leeds (Mr. James E. Bedford) have become Honorary Vice-Presidents of the British Empire Industrial League.

Society of Public Analysts and other Analytical Chemists.—A joint meeting of the Society and the Biochemical Society will be held on Wednesday, May 5th, at the Chemical Society's Rooms, Burlington House, Piccadilly, W., at 8 p.m. The meeting is to be devoted to a discussion of "Methods adopted in the Estimation of the Nitrogenous Constituents of Extracts derived from Albuminous Substances, such as Meat Extracts and similar products, with special reference to the interpretation of the results." Sir William Crookes, O.M., F.R.S., and Prof. Raphael Meldola, F.R.S., will be balloted for as honorary members, and there are four candidates for ordinary membership of the Society. It is suggested that members of the two Societies should dine together before the meeting at the Hotel Previtali, Arundell Street, Piccadilly Circus, at 6.15 o'clock. The Honorary Secretaries will be obliged if members who propose attending the dinner will notify Mr. E. RICHARDS BOLTON, 46, Stamford Brook Road, W., as soon as possible, in order that arrangements may be made.

The "Van 't Hoff Fund."—In agreement with the regulations of the "Van 't Hoff Fund," founded on June 28, 1913, persons interested are informed herewith of the following particulars:—The foundation, whose residence is Amsterdam, and of which the supervision is vested in the Royal Academy of Sciences there, is appropriated to give from the rents of the fund every year, before March 1st, endowments to investigators in the field of pure and applied chemistry who will have applied for such an endowment before November 1st preceding the above-mentioned date to the Committee charged with considering the applications and awarding the grants. Momentarily this Committee is constituted as follows:—A. F. HOLLEMAN (President), S. Hoogewerff, A. Smits, F. M. Jaeger (Secretary). If desirable this Committee may appoint

still other members, for one year only, to co-operate in judging of the applications made. The names of persons to whom a grant is allowed will be published. The grantees are requested to send to the Committee some copies of the papers relating to the results of their work, but for the rest they are at liberty to choose the manner of publication as well as the journal in which they like to publish their results, if only they mention the fact that the research was made with an endowment from the "Van 't Hoff Fund." The amount available over 1916 is about £108 (520 dols.). Applications should be sent, registered by post, to Het Bestuur der Koninklijke Akademie van Wetenschappen, bestemd voor de Commissie van het "Van 't Hoff-Fonds," Trippenhuis, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant and of the reasons on which the candidates ground their claim. An endowment was made in 1915 to Dr. D. E. Tsakalotos, in Athens (Greece), to an amount of 600 francs, for his investigations on the viscosity and magnetism of binary mixtures, which can deposit endothermic compounds.—In the name of the Committee of the "Van 't Hoff Fund," A. F. HOLLEMAN (President), P. M. JAEGER (Secretary).—Amsterdam, April, 1915.

## MEETINGS FOR THE WEEK.

- MONDAY, May 3rd.—Royal Institution, 5. Annual Meeting.  
Royal Society of Arts, 8. (Cantor Lecture).  
"Food-stuffs," by David Sommerville, B.A., M.D.
- TUESDAY, 4th.—Royal Institution, 3. "The Animal Spirits," by Prof. C. S. Sherrington, F.R.S.  
Royal Society of Arts, 4.30. "The Empire's Resources in Paper-making Materials," by S. C. Phillips.
- WEDNESDAY, 5th.—Royal Society of Arts, 8. "Measurement of the Efficiency of Domestic Fires, and on a Simple and Smokeless Grate," by A. Vernon Harcourt, F.R.S.  
Society of Public Analysts, 8. Discussion of "Methods adopted in the Estimation of Nitrogenous Constituents of Extracts derived from Albuminous Substances, such as Meat Extracts and similar Products, with special reference to the Interpretation of the Results."
- THURSDAY, 6th.—Royal Institution, 3. "Advances in General Physics," by Dr. A. W. Porter, F.R.S.  
Royal Society of Arts, 4.30. "Constantin Meunier et les Sculpteurs Belges de son Temps," by Paul Lambotte.  
Royal Society. "Some Problems illustrating the Forms of Nebulae," by G. W. Walker. "Observations on the Resonance Radiation of Sodium Vapour" by Hon. R. J. Strutt. "Local Differences of Pressure near an Obstacle in Oscillating Water," by Hertha Ayrton. "Measurement of the Specific Heat of Steam at Atmospheric Pressure and 104.5° C.," by J. H. Brinkworth. "Thermal Properties of Carbonic Acid at Low Temperatures," by C. F. Jenkin and D. R. Pyle.  
Chemical, 8.30. "Rotatory Dispersive Power of Organic Compounds—Part VI., Complex Rotatory Dispersion in Ethyl Tartrate," by T. M. Lowry and T. W. Dickson; Part VII., "Complex Rotatory Dispersion in Methyl Tartrate," by T. M. Lowry and H. H. Abram. "Experiments on Supersaturated Solutions," by M. Jones and J. R. Partington. "Sulphonyl and Carbonyl Derivatives of Alanine—Resolution of Externally Compensated  $\beta$ -Toluenesulphonylalanine into its Optically Active Components," "The Resolution of Externally Compensated Tetrahydro- $\beta$ -naphthoquinoline into its Optically Active Components," and "The Non-resolution of *dl*-Tetrahydro- $\beta$ -naphthoquinoline by means of *d*-Oxymethylene-camphor," by C. S. Gibson and J. L. Simonsen. "Syntheses with the Aid of Monochloromethyl Ether—Part III., The Action of Monochloromethyl Ether on the Sodium Derivatives of Ethyl Ethane- $\alpha$ - $\beta$ -tricarboxylate, Ethyl Butane- $\alpha$ - $\beta$ -tetracarboxylate, and Ethyl Pentane- $\alpha$ - $\gamma$ - $\delta$ -tetracarboxylate," by J. L. Simonsen. "Nitration of 3-Acetylamino-2-methoxy Toluene" and "Condensation of Ethylcyanoacetate and Acetyl Acetone," by J. L. Simonsen and M. Nayak.
- FRIDAY, 7th.—Royal Institution, 9. "Electrons and Heat," by Prof. O. W. Richardson, F.R.S.
- SATURDAY, 8th.—Royal Institution, 3. "Photo-Electricity (Experimental)," by Prof. J. A. Fleming, F.R.S.



# THE CHEMICAL NEWS.

VOL. CXI., No. 2893.

## THE SEPARATION OF THE ALKALINE EARTH METALS AND THE ALKALIS.

By ROBERT GILMOUR.

THE following scheme for the separation of the alkaline earth metals and alkalis has been found to give excellent results in practice, and can be recommended as a good working method. It is based on the fact that calcium potassium ferrocyanide is very sparingly soluble, whilst the corresponding strontium compound is easily soluble (Bottger, "Qualitative Analyse").

### Group IV.

Evaporate the filtrate from the iron group to complete dryness, and ignite to expel ammonium salts. Dissolve the residue in 10 cc. of water with the addition of one or two drops of dilute HCl, if necessary, and filter from any carbonaceous matter. Heat to boiling. Add 5 cc. of  $\text{NH}_4\text{Cl}$ , 5 cc. of  $\text{NH}_4\text{OH}$ , and 10 cc. of  $(\text{NH}_4)_2\text{CO}_3$ . Keep near the boiling-point for a few minutes, filter, and wash the precipitate.

*Filtrate.*—Group V.

*Precipitate.*—Carbonates of Ba, Sr, and Ca.

Dissolve in hot acetic acid, using not more than 3 to 4 cc. Neutralise with ammonia, and add an excess of 2 cc. of acetic acid. Dilute the solution to 15 to 20 cc., heat to boiling, and add  $\text{K}_2\text{CrO}_4$  solution until the liquid assumes an orange colour (10 cc. should be ample). Keep near the boiling-point for two or three minutes, and filter.

*Precipitate, P<sub>1</sub>.*— $\text{BaCrO}_4$ .

Wash with water, moisten with dilute HCl, and confirm Ba by flame coloration.

*Filtrate, F<sub>1</sub>.*

Heat to boiling, and add  $(\text{NH}_4)_2\text{CO}_3$  solution until the orange colour of the liquid changes to yellow. Then add an excess of 4 to 5 cc. Keep hot for a few minutes, filter, and wash.

*Filtrate, F<sub>2</sub>.*—Neglect.

*Precipitate, P<sub>2</sub>.*— $\text{SrCO}_3$  and  $\text{CaCO}_3$ .

Dissolve in a small quantity of hot acetic acid, and make alkaline with ammonia. (The solution should now occupy not more than 4 to 5 cc.)

Divide the solution into two parts, and test for Sr and Ca as follows:—

(i.). Add an equal volume of saturated  $\text{CaSO}_4$  solution, and boil for a few minutes. A white crystalline precipitate or turbidity indicates *strontium*. Filter, and confirm by flame coloration.

(ii.). Add an equal volume of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution, and boil. A white crystalline precipitate or turbidity appearing in a minute or two indicates *calcium*.

(A saturated solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  is advisable, but the ordinary bench solution gives satisfactory results in most cases).

(NOTE.—Before proceeding with the separation of the metals of the group, the solution should be tested for Ba by adding  $\text{K}_2\text{CrO}_4$  to a very small portion).

If Ba is present the analysis is carried out according to the scheme.

If Ba is absent the precipitate, if any, obtained with  $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$  is treated in the same manner as precipitate  $\text{P}_2$  in the above scheme.

### Group V.—Mg, Na, and K.

Concentrate the filtrate from Group IV. to about 10 cc. Add 4 to 5 cc. of  $(\text{NH}_4)_2\text{CO}_3$  and 15 cc. of alcohol, and allow to stand for fifteen minutes. (Rub the interior of

the vessel with a glass rod to induce crystallisation, if necessary).

*Precipitate.*— $\text{MgCO}_3(\text{NH}_4)_2\text{CO}_3$ .

Magnesium may be confirmed by dissolving the precipitate in a few drops of dilute HCl, and adding  $(\text{NH}_4)_2\text{HPO}_4$ . A white crystalline precipitate indicates magnesium.

*Filtrate.*—Na and K.

Identify in the usual manner.

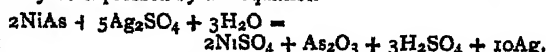
Chemistry Department,  
University of Edinburgh.

## STUDIES IN SILVER ENRICHMENT.\*

TETRANICKEL-TRIARSENIDE, ITS CAPACITY AS SILVER PRECIPITANT.

By CHASE PALMER.

THE precipitation of free silver by the interaction between many metallic minerals and dilute silver sulphate solution has been described in detail by Palmer and Bastin in an introductory chapter of their studies in silver enrichment (Palmer, Chase, and Bastin, "Metallic Minerals as Precipitants of Silver and Gold," *Economic Geology*, 1913, viii., 140). Noteworthy among silver precipitants is the nickel monarsenide, niccolite ( $\text{NiAs}$ ). Quantitative experiments have shown that, coincident with the deposition of silver, the substance niccolite is completely dissolved as nickel sulphate and arsenious acid, and that the proportions of the substances involved in the reaction may be expressed by the equation—



Thus 1 grm. of niccolite is capable of precipitating 4.02 grms. of metallic silver.

Inasmuch as this property of niccolite may have a direct bearing on the origin of rich silver deposits such as are found in the Canadian cobalt district, where arsenides of cobalt and nickel abound, the study of the precipitation capacities of other arsenides and similar minerals has been undertaken to determine to what extent arsenides and antimonides in general share with niccolite the power to precipitate silver from silver salt solutions. Of the several minerals that have been studied quantitatively with respect to their conduct towards silver solutions, one in particular deserves special mention. It was obtained from a well known company of mineral dealers, and purported to be chloanthite ( $\text{NiAs}_2$ ), from Mansfeld, Thuringen, Germany. The material is light grey with a tinge of red. Weighed quantities of the powdered mineral were digested in dilute silver sulphate solutions. As in the case of niccolite action began promptly, an abundant silver deposit was soon formed, and the solution became green. The results of the experiments recorded below show conclusively that the mineral cannot be chloanthite ( $\text{NiAs}_2$ ) nor Rammelsbergite ( $\text{NiAs}_2$ ), which it closely resembles, but is a wholly different substance, which, according to the atomic proportions of its soluble constituents, may be called tetranickel-triarsenide ( $\text{Ni}_4\text{As}_3$ ).

EXPERIMENT I.—*Action of the Mineral with an Aqueous Solution containing a large Excess of Silver Sulphate.*—The finely powdered mineral (0.363 grm.) was digested over night in about 750 cc. of a solution containing 3.8 grms. silver sulphate. Silver soon began to deposit in beautiful white arborescent crystals. After twelve hours the small amount of dark residue, together with the abundant silver deposit, was filtered from the green solution. The deposit contained 1.4089 grms. metallic silver. After its removal the residue yielded:—

\* Second communication in a series of geological and chemical co-operative studies by Bastin and Palmer. Published by permission of the Director of the U.S. Geological Survey. Reprinted from *Economic Geology*, iv., No. 7.

0.0093 gr.  $\text{Bi}_2\text{S}_3$  = Bi 2.55 per cent.  
 0.0111 gr.  $\text{BaSO}_4$  = S 0.42 per cent.  
 0.0008 gr.  $\text{Fe}_2\text{O}_3$  = Fe 0.15 per cent.  
 0.0034 gr. gangue = 0.93 per cent.

and from the solution were obtained :—

0.1726 gr. Ni = Ni 47.55 per cent.  
 0.0045 gr. Co = Co 1.24 per cent.  
 0.2809 gr.  $\text{As}_2\text{S}_3$  = As 47.05 per cent.

99.89 per cent.

Atomic proportions of the dissolved constituents :—

$47.55 \div 58.7 = 0.8101$   
 $1.24 \div 59.0 = 0.0210$  }  $0.8311 \text{ Ni (Co)}$   
 $47.05 \div 75.0 = 0.6273$  As

and  $0.8311 : 0.6273 = 3.98 : 3 = \text{Ni}_4\text{As}_3$ .

These results show that the substance dissolved by the silver sulphate solution constitutes 95.84 per cent. of the material under examination, and that the empirical formula,  $\text{Ni}_4\text{As}_3$ , represents the atomic proportions of the constituents of the dissolved mineral.

Ratio of precipitated silver and the mineral ( $\text{Ni}_4\text{As}_3$ ).  
 0.363 grm. material contains 0.352 grm.  $\text{Ni}_4\text{As}_3$  (mol. wt. 459.8).

Percentage.

$388.12 \div 107.9 = 3.5970 \text{ Ag,}$   
 $95.84 \div 459.8 = 0.2084 \text{ Ni}_4\text{As}_3,$

and  $3.5970 : 0.2084 = 17 : 1$ .

Thus tetranickel triarsenide precipitates silver in the proportion of 1 molecule to 17 atoms of silver. In other words, 1 grm. of this nickel arsenide has the capacity of depositing 3.99 grms. of metallic silver.

EXPERIMENT 2.—*Action of the Mineral with an Aqueous Solution containing a Deficiency of Silver Sulphate.*—The possibility that the material dissolved by silver sulphate solution might be a mixture of normal nickel arsenide ( $\text{Ni}_3\text{As}_2$ ) and niccolite ( $\text{NiAs}$ ) in molecular proportions was considered, and to obtain light on this question an experiment in fractional oxidation was tried.

The powdered mineral (0.4006 grm.) was digested twelve hours in 500 cc. of a solution containing 1.52 grms. silver sulphur sulphate. In this time 1.045 grms. metallic silver—that is, 260.9 per cent of the weight of the material used—had been precipitated, and 0.2628 grm.—that is, 65.6 per cent of the material—was dissolved, the dissolved constituents being distributed as follows :—

Ni(Co),  $0.1334 \text{ grm.} = 33.30 \text{ per cent.}$   
 As,  $0.1294 \text{ grm.} = 32.30 \text{ per cent.}$   
 $0.2628 \text{ grm.} = 65.60 \text{ per cent.}$

Atomic proportions of the dissolved constituents :—

Percentage.  
 $33.30 \div 58.7 = 0.5683 \text{ Ni(Co),}$   
 $32.30 \div 75.0 = 0.4306 \text{ As,}$

and  $0.5683 : 0.4306 = 3.96 : 3$ .

Ratio of precipitated silver and dissolved mineral :—

Percentage.  
 $260.9 \div 107.9 = 2.4179 \text{ Ag,}$   
 $65.6 \div 459.8 = 0.1431 \text{ Ni}_4\text{As}_3,$

and  $2.4179 : 0.1431 = 16.9 : 1$ .

Thus, also, when the mineral is only partially oxidised, four atoms of nickel and three atoms of arsenic enter the solution together, and seventeen atoms of silver are deposited. Additional evidence therefore is obtained that the soluble mineral is a definite substance and not a mixture of two substances.

Prior to these observations, which were made in January, 1914, F. Grünling ("Maucherit, ein neues

Nickelmineral," *Centralblatt für Mineralogie, Geologie, und Paläontologie*, April 15, 1913, p. 225) announced the discovery by W. Maucher of a new silver-white nickel arsenide. From the chemical analyses accompanying his description of the mineral, Grünling assigned to it the formula for normal nickel arsenide,  $\text{Ni}_3\text{As}_2$ , and he named it "maucherite." In February, 1914, T. L. Walker ("Temiskamite, a New Nickel Arsenide from Ontario," *Amer. Journ. Sci.*, 4th ser., vol. xxxvii., p. 170) reported a new mineral received from the Cobalt district, Ontario. The description of the physical properties of Walker's Ontario mineral closely corresponds to the description of the properties of Grünling's maucherite, but Walker interpreted the analytical results obtained from his mineral as indicative of tetranickel-triarsenide ( $\text{Ni}_4\text{As}_3$ ). In view of these two recent observations and of the writer's conclusions concerning the real chemical proportions of nickel and arsenic in the specimen which he received for chloanthite, but which by means of the silver sulphate solution was found to be tetranickel-triarsenide, it seemed desirable to make a comparative study of all three substances. In response to requests, Prof. Grünling and Prof. Walker generously contributed supplies of their minerals, so that this work could be done.

EXPERIMENT 3.—*With Maucherite, Grünling's Mineral from Eisleben, Thuringen.*—Silver-white grains of maucherite were carefully selected, finely ground, and the heavy material was separated from gangue by methylene iodide. The mineral (0.3992 grm.) was digested over night in 750 cc. of an aqueous solution containing 3.12 grms. silver sulphate. 1.5702 grms. silver was deposited, equivalent to 393.3 per cent of the weight of the material taken.

The residue also yielded :— 0.05 per cent S,  
 0.27 per cent Bi,  
 0.04 per cent Fe,

and from the solution were obtained :—

$0.1942 \text{ grm. Ni} = 0.81 \text{ per cent gangue,}$   
 $0.0052 \text{ grm. Co} = 1.32 \text{ per cent Co,}$   
 $0.3172 \text{ grm. As}_2\text{S}_3 = 48.50 \text{ per cent As.}$   
 99.79

The atomic ratios of the dissolved constituents are :—

Percentage.  
 $48.80 \div 58.7 = 0.8313 \text{ Ni}$   
 $1.32 \div 59.0 = 0.0223 \text{ Co}$  }  $0.8536 \text{ Ni(Co)}$   
 $48.50 \div 75.0 = 0.6467 \text{ As}$   
 98.62

and  $0.8536 : 0.6467 = 3.96 : 3$ .

From these calculations it is evident that the nickel arsenide, called maucherite, constitutes nearly 99 per cent of the material under examination, and has the empirical formula  $\text{Ni}_4\text{As}_3$ .

Ratio of precipitated silver and  $\text{Ni}_4\text{As}_3$ —

Percentage.  
 $393.8 \div 107.9 = 3.645 \text{ Ag,}$   
 $98.62 \div 459.8 = 0.2144 \text{ Ni}_4\text{As}_3,$

and  $3.645 : 0.2144 = 17 : 1$ .

Thus this nickel arsenide has the same capacity for precipitating metallic silver as has the miscalled "chloanthite" which has already been reviewed.

C. Friedrich's analytical results of the chief constituents, as stated by Grünling in his description of the mineral, are Ni 49.51 per cent, Co 0.93 per cent, and As 45.66 per cent; total, 96.10 per cent, of which the atomic ratios are :—

$$\begin{aligned} 49.51 \div 58.7 &= 0.8434 \\ 0.93 \div 59.0 &= 0.0157 \\ 45.66 \div 75.0 &= 0.6088 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} 0.8591 \text{ Ni(Co),}$$

and  $0.8591 \div 0.6088 = 4.23 : 3$ .

It thus appears that Freidrich's results conform to the formula  $\text{Ni}_4\text{As}_3$  about as closely as to the formula  $\text{Ni}_3\text{As}_2$ .

EXPERIMENT 4.—With Walker's "Temiskamite" from Elk Lake, Ontario.—The material was carefully selected, run through a 100-mesh sieve, and the powder separated as far as possible from gangue by methylene iodide. The weighed mineral was digested for two days with 600 cc. of a solution containing 2.33 grms. silver sulphate.

0.4018 gm. mineral precipitated,  
1.4937 grms. free silver.

From the residue were also obtained :—

0.0065 gm. Co = 1.61 per cent Co,  
0.0161 gm.  $\text{Mg}_2\text{As}_2\text{O}_7$  = 1.94 per cent As,  
0.0255 gm.  $\text{BaSO}_4$  = 0.87 per cent S,  
0.0200 gm.  $\text{Bi}_2\text{S}_3$  = 1.99 per cent Bi,  
Gangue = 0.64 per cent.

And from the solution were obtained :—

0.1916 gm. Ni = 47.69 per cent Ni,  
0.0017 gm. Co = 0.42 per cent Co,  
0.2951 gm.  $\text{As}_2\text{S}_3$  = 44.65 per cent As.  
99.81

Atomic ratios of the constituents found in the residue :—

$$\begin{aligned} 1.61 \div 59 &= 0.0273 \text{ Co} = 1 \\ 1.94 \div 75 &= 0.0259 \text{ As} = 1 \\ 0.87 \div 32 &= 0.0271 \text{ S} = 1 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{CoAsS,}$$

and of the dissolved constituents :—

$$\begin{aligned} 47.69 \div 58.7 &= 0.8124 \\ 0.42 \div 59.0 &= 0.0007 \\ 44.65 \div 75.0 &= 0.5953 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} 0.8131 \text{ Ni(Co),}$$

and  $0.8131 \div 0.5953 = 4.11 : 3 = \text{Ni}_4\text{As}_3$ .

This oxidation experiment shows, not only that the chief homogeneous substance in the Canadian product is tetranickel triarsenide, but also that a substance answering to cobaltite is present in appreciable amount. The bismuth appears to be in the metallic state. From all the analytical data obtained by this experiment the natural product may be considered to be a mixture consisting essentially of :—

92.76 per cent tetranickel-triarsenide ( $\text{Ni}_4\text{As}_3$ ),  
4.42 per cent cobaltite ( $\text{CoAsS}$ ),  
1.99 per cent bismuth,  
0.64 per cent gangue.

99.81

Ratio of the Canadian tetranickel-triarsenide and precipitated silver :—

Percentage.

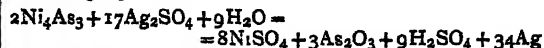
$$\begin{aligned} 371.7 \div 107.9 &= 3.4448 \text{ Ag,} \\ 92.76 \div 459.8 &= 0.2017 \text{ Ni}_4\text{As}_3, \end{aligned}$$

and  $3.4448 \div 0.2017 = 17.08 : 1 = 17\text{Ag} : \text{Ni}_4\text{As}_3$ .

This experiment also shows that 1 gm. of tetranickel-triarsenide is capable of precipitating practically 4 grms. of metallic silver.

The silver precipitation capacity of this Canadian product, like that of the misnamed chloanthite from Mansfeld and of Grünling's maucherite from Eisleben, depends on the amount of tetranickel-triarsenide contained in it. Since in every instance one molecular weight of the nickel arsenide ( $\text{Ni}_4\text{As}_3$ ) is capable of precipitating silver in the weight proportion of 17 atoms, and since the oxidation

product is limited to arsenious acid, the proportional amounts of the substances participating in the reaction with silver sulphate solution may be expressed by the following equation :—



A striking feature of all these experiments is the definiteness of the reaction between tetranickel-triarsenide and silver sulphate solution, and it recalls the reaction between silver sulphate solution and niccolite, which is of the same order of regularity.

Since tetranickel-triarsenide was first observed as a new species by Maucher, it seems appropriate that *Maucherite*, the name given to it by Grünling, be retained.

#### *Maucherite, from Mansfeld, Thuringen.*

*Properties.*—Cleavage imperfect, fracture uneven, brittle, hardness 5, specific gravity 7.80, lustre metallic, colour white with red tarnish, streak black, not magnetic, opaque, fusibility 2. Soluble in strong nitric acid, with evolution of nitrous fumes. Closed tube, slight deposit of arsenious oxide. Open tube, abundant deposit of arsenious oxide. On charcoal, white arsenic coating. This description of tetranickel-triarsenide from Mansfeld applies equally well to Walker's Canadian specimen and to Grünling's maucherite from Eisleben. Moreover, freshly polished surfaces of all three specimens, observed under the reflecting microscope by daylight, showed that a radiating fibrous structure is common to all, and that all have exactly the same silver-grey colour. For specific gravity determinations by the standard pyknometer method of the U.S. Geological Survey the writer is indebted to George Steiger. The determinations were made at 25° C. on the powdered materials as they were used for the experiments described in this paper. For comparison the tabulation is in descending order of maucherite content :—

	Grünling's Mineral.	Palmer's Mineral.	Walker's Mineral.
Per cent. $\text{Ni}_4\text{As}_3$	98.62	95.84	92.76
Specific gravity..	7.81	7.80	7.73

#### *Crystallography.*

*Tetragonal.*—The three specimens of maucherite used in these experiments are all of the massive variety, with nothing indicative of crystalline form. Very recently, however, A. Rosati ("Über Maucherit und Placodin," *Zeit. Kryst. Min.*, 1914, liii., 389) has reported the results of an exhaustive investigation of the crystallography of Grünling's maucherite, his results being based largely on new material supplied by Maucher himself. According to Rosati maucherite is tetragonal, its usual form being in thin quadratic plates parallel to the base, with the other faces strongly striated.

#### *Thuringian Maucherite.*

In the Mansfeld mining district, Thuringen, not far from Eisleben, where Grünling's maucherite was found, is the "Sangerhäuser Reviere" (so called by Bäumler), long famous for its rich output of nickel ores. In an extensive report on the nickel ores of that district in 1857 Bäumler stated that the prevailing variety of niccolite at Sangerhausen was faintly lustrous and had a touch of grey ("Über das Vorkommen von Nickelerzen im Mansfeldschen Kupferschiefergebirge," *Zeit. Deutsch. geol. Gesellsch.*, 1857, ix., 25). This paleness Bäumler ascribed to chloanthite ( $\text{NiAs}_2$ ) and cobaltite ( $\text{CoAsS}$ ), mechanically admixed with true niccolite ( $\text{NiAs}$ ). Grunow's (*Zeit. Deutsch. geol. Gesellsch.*, 1857, ix., 40) analysis of the product does not conform to this view, which demands that the ratio of the percentage values of nickel and arsenic should be larger than it is in niccolite, whereas it is much smaller; in fact, it is the ratio appertaining to tetranickel-triarsenide ( $\text{Ni}_4\text{As}_3$ ).

Composition of the Sangerhausen ore according to Grunow.

Ni(Co?), 48.4 per cent.  
As, 48.7 per cent.  
S, 2.8 per cent.

99.9

In the light of our present knowledge of the occurrence of Grunling's maucherite in the neighbouring mines at Eisleben, and Palmer's Mansfeld maucherite it is possible that the faintly lustrous nickel arsenide, considered by Bäumler to be a variety of niccolite, was really tetranickel-triarsenide; that is, maucherite, with mechanically admixed cobaltite or its nickel homologue, and that the pale ore examined by Grunow consisted essentially of 85.4 per cent maucherite ( $\text{Ni}_4\text{As}_3$ ) and 14.5 per cent cobaltite ( $\text{CoAsS}$ ).

From these considerations it may be suspected that tetranickel-triarsenide has formed a not inconsiderable part of the output of the Mansfeld mining district.

In addition to the above described experiments with maucherite, quantitative oxidation experiments have been made likewise with several arsenical minerals, including niccolite ( $\text{NiAs}$ ), smaltite ( $\text{CoAs}_2$ ), cobaltite ( $\text{CoAsS}$ ), and arsenopyrite ( $\text{FeAsS}$ ), and a few deductions from these experiments may be stated in a brief summary.

#### Summary.

1. The mineral, maucherite, tetranickel-triarsenide ( $\text{Ni}_4\text{As}_3$ ), containing the largest proportion of nickel of all nickel arsenides known, is a homogeneous substance. It appears to be rather widely distributed, for within one year it has been found on two continents.
2. Silver sulphate solution is an efficient solvent of pure arsenides preparatory to analysis.
3. In sulpharsenides, preferably called arsenosulphides, sulphur appears to functionate atomically with arsenic, the arsenosulphide group ( $\text{AsS}$ ) being strongly resistant to the oxidising action of silver salt solutions. Sulphur, therefore, may be regarded as a protector of arsenic against oxidation by silver salt solutions.
4. In regions abounding in deposits of native silver associated with arsenical minerals the source of the silver should be attributed to the action of arsenides rather than of arsenosulphides, such as arsenopyrite ( $\text{FeAsS}$ ), and cobalt arsenosulphide ( $\text{CoAsS}$ ); that is, cobaltite on silver salt solutions.
5. The silver precipitation capacity of a nickel or cobalt arsenide depends on the proportional amount of arsenic uncombined with sulphur; that is, the arsenic of simple arsenides.

The study of ore enrichment involves problems the solution of which requires a knowledge of the chemical properties of the homogeneous substances contained in many mineral mixtures, and there is much to be learned concerning the conduct of ore-forming minerals with metallic salt solutions which may come in contact with them. In future, if as much attention is paid to the chemical conduct of minerals as has been directed hitherto to their total content, and to the determination of their physical properties, there is reason to believe that chemical mineralogy will become a more systematic and serviceable branch of mineralogical science than it is to-day.

Institute of Metals May Lecture.—Sir J. J. Thomson O.M., D.Sc., F.R.S., will deliver this year's Institute of Metals May Lecture, his subject being "The Passage of Electricity Through Metals." The lecture will be given at the Institution of Electrical Engineers on Wednesday, May 12, at 8.30 p.m. Visitors' tickets can be obtained on application to Mr. G. Shaw Scott, M.Sc., the Secretary of the Institute of Metals, Caxton House, Westminster, S.W.

#### RECOVERY OF MOLYBDIC ACID.\*

By W. D. BROWN.

On account of the rise in price of molybdic acid, an attempt was made in the Duquesne Laboratory last May to recover it from the filtrates from determinations of phosphorus. Various methods were tried before the present one was settled upon as giving the best recovery with the least work and expense. The method consists of the precipitation of the molybdic acid from the ferric nitrate solution with an excess of phosphate. At first the theoretical amount of phosphorus was added to the cold solution and but one-third the molybdic acid was recovered. At the present time five times the theoretical amount of phosphate is added to the boiling solution.

It has been the practice in this laboratory to make the acid in  $\frac{1}{2}$  lb. lots of 85 per cent molybdic acid, making 3500 cc. of solution and in agreement with the adopted method of the U.S. Steel Corporation. The filtrates from 3500 cc. of ammonium molybdic solution are heated to boiling and a solution containing 200 grms. commercial sodium phosphate added. The precipitate is allowed to settle and, after the solution is decanted, is transferred to a large-mouthed bottle. When sufficient yellow precipitate from several precipitations is obtained, it is washed by decantation, transferred to a dish, the water evaporated off, and the precipitate dried on a sand bath.

According to the commonly accepted formula for the yellow precipitate, it contains 92 per cent  $\text{MoO}_3$ , and 210 grms. would contain the same weight of acid as  $\frac{1}{2}$  lb. of 85 per cent molybdic acid. Accordingly, for the precipitation of the molybdic acid solution, 210 grms. of yellow precipitate are weighed and 800 cc. water added, followed by 600 cc. ammonia. The solution is cooled and 35 grms. magnesium nitrate, dissolved in 100 cc. water, are added to precipitate all the phosphorus. After the solution has stood for some time it is filtered and the precipitate is washed with 100 cc. water or dilute ammonia. The filtrate is added to 1900 cc. of 1:1 nitric acid, the total volume being 3500 cc., and containing the usual amount of ammonia and nitric acid.

In this laboratory the recovery has been only about 85 to 87 per cent. The cost of recovery of one pound of molybdic acid is about 10 cents: 7 cents for the sodium phosphate and 3 cents for the magnesium nitrate, the ammonia being required in the ammonium molybdate solution.

#### PHOTOSYNTHESIS IN ORGANIC CHEMISTRY.†

##### INTRODUCTION AND GENERAL CONSIDERATIONS.

By E. PATERNO.

(Continued from p. 210).

THE influence of light on etherification has not been systematically studied; facts, however, are known where the etherification of an acid with an alcohol at a given temperature does not take place in the dark but does so in the light. Examples of it are the etherification of cinnamic acid and of opianic acid, observed by Ciamician and Silber.

The oxidation and reduction phenomena which light provokes or quickens have been largely studied, but it would be an almost hopeless task to write their history, since they are so mingled with the photographic studies, where numerous applications of them have been made.

If we restrain ourselves to the purely chemical transformations, I have already said how Berthollet had interpreted the experiences of Rumford, admitting that the hydrogen of the organic substances (ether, turpentine,

\* Presented before the Pittsburgh Section of the American Chemical Society, January 21, 1915. From the *Journal of Industrial and Engineering Chemistry*, vii, No. 3.

† From the *Gazzetta Chimica Italiana*, 1909-1914.

oils) acts as the reducing agent; we saw, too, that since 1725 the reduction of ferric chloride by ether had been observed. The reducing properties of the alcohols rendered more active by light have been utilised step by step in the development of chemistry; in some acids too, as oxalic and formic acid, the same properties have been later found and studied, and of other substances, as aldehyde and hydroxylamine, the reducing power was acknowledged as soon as they were discovered. On the other side, the oxidation in the air of some substances under the action of light, which is generally accompanied by the formation of hydrogen peroxide (Richardson and Fortey, *Trans. Chem. Soc.*, lix., 51; lxx., 450; lxxx., 1349), has been the object of important studies, and it has been observed that mineral salts (especially uranium salts) have an influence on the velocity of the phenomenon (Fay, *loc. cit.*; Bargellini and Mieli, *Gazz. Chim. Ital.*, 1907, xxxvii., 417).

But besides the reductions of the metallic salts brought about by organic substances, and besides the corresponding oxidation of these substances by salts or by atmospheric oxygen, other and very important reactions have been studied, which take place under the action of solar rays, between two different organic substances, the one of which is reduced, the other oxidised; in particular, the reducing action of alcohols on organic substances has been fully studied.

The first who undertook studies in this direction was Klinger, who in the *Sitzungsberichten der Bonn Gesellschaft für Natur und Heilkunde*, in 1883 and in 1885, made known the results he had obtained by exposing to the light benzyl and phenanthraquinone together with alcohol, and showed that the alcohol is oxidised to aldehyde, while the phenanthraquinone gives the corresponding hydroquinone, and the benzyl gives a reduction product. These results were published in the *Berichte of Berlin* in 1886 (*Ber.*, xxix., 1864 and 1869).

Almost at the same time as this last paper, Ciamician proved that quinone under the same conditions is transformed into hydroquinone (*R. Acc. Lincei*, Meeting of January 3, 1886; *Gazz. Chim. Ital.*, xvi., 111; *Ber.*, xix., 551). Later on, Ciamician and Silber found that nitrobenzene is reduced to quinaldine (*Ber.*, xix., 2899), and Klinger in a paper issued in the *Liebig's Annalen* (1888, ccxlix., 137) extended his experiments, giving them a much greater bearing; showing that acetic aldehyde combines itself with phenanthraquinone, giving the monomethylphenanthraquinhydrone, thus performing, as he says, the first synthesis by means of light; similar reactions he got with isovaleric and benzoic aldehydes.

A short time after, in 1890, Echsner de Koninck and Darrien (*Comptes Rendus*, cxxx., 1768) observed that ketones too are reduced by alcohol, and made the experiment with benzophenone and acetophenone, as, indeed, Klinger himself had already done with a diketone (viz., benzyl).

To our knowledge on the reducing action of alcohols on quinones and on ketones Ciamician and Silber brought from 1902 to 1906 a very valuable contribution; they have proved that the transformation of quinone into hydroquinone takes place with all the compounds with alcoholic groups, such as glycerol, erythritol, mannitol, dulcitol, glucose, and that other quinones, as thymoquinone, react in the same way.

They have also proved that reduction of quinone to hydroquinone is also accomplished by some acids (formic, acetic, propionic), and by hydrocarbons (petroleum ether).

The readiness with which alcohols give up their hydrogen to transform themselves into the corresponding aldehydes, which the action of direct light still more accentuates, manifests itself also by the effect of temperature alone, and it will be enough to quote the method of Trillat for the preparation of formic aldehyde from methyl alcohol, and, above all, the important studies of Ipatiew. This chemist has proved that with common alcohol (at 800° to 820°) and with butylic and allylic alcohol, the corresponding aldehydes are formed, and with isopropyl-

alcohol, acetone (*Ber.*, 1901, xxxiv., 3579; xxxv., 1047, 1057; xxxvi., 1990, 2003, 2014, 2016, &c.).

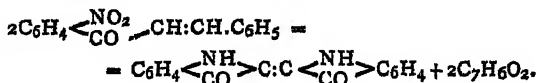
Ciamician and Silber, moreover, explaining the mechanism of the reaction between alcohol and benzophenone, as observed by Echsner and Darrien, showed that the reaction proceeds in quite the same manner as the transformation of benzyl studied by Klinger, and benzopinacol is therefore formed, and by a similar reaction they obtained from benzoic aldehyde hydrobenzoin, from anisic aldehyde hydroanisoin, and from benzoin hydrobenzoin.

But the work of Ciamician and Silber is not limited only to the detailed study of the reduction of quinones and ketones. They have obtained by the action of alcohol on nitrobenzene and on nitrotoluene, together with aniline and toluidine, quinaldine and methylquinaldine, from isatine hydroisatine, from alloxane alloxantine.

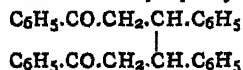
The synthetical reactions obtained by means of light are, indeed, not very numerous. While we will give a more complete classification later on, a first class is that which comprehends the synthesis by polymerisation. Two noteworthy instances of it are the transformation of bromoacetylene into tribromobenzene and of propiolic into trimelic acid (Baeyer, *Ber.*, xix., 2185).

Klinger, as we have seen above, attributes to himself the first synthesis, but it is only formation of an ether, and not the direct linking of carbon to carbon.

Other syntheses, whose type is that observed by Klinger in the transformation of benzil into benzoylbenzoin, and which are all parallel among themselves, are those of the transformation of quinones into quinhydrone, of ketones into pinakones, of aromatic aldehydes in hydrobenzoin, hydroanisoin, of alloxane into alloxantine; in all of which we have a reduction with a subsequent union of the reduced product, molecule to molecule, with the first one. But these reactions, which take place in a simple enough manner by the action of hydrogen, if they confirm the reducing power of the alcohols under the action of solar rays, present nothing new or particularly interesting from the point of view of synthesis in organic chemistry; so that, excluding the syntheses by polymerisation above mentioned, the first real synthesis by the action of light is, according to our opinion, that of indigo made by Engler and Dorant, in 1895 (*Ber.*, xxviii., 2497), from benzyldien-*o*-nitro-acetophenone:—



Other important syntheses are:—That of dehydrovanillin from vanillin, where we pass from a benzene derivative to one of diphenyl (Ciamician and Silber, *Gazz. Chim. Ital.*, 1902, i., 218), that of triphenylglycol by the addition of benzyl alcohol to benzophenone (*Gazz. Chim. Ital.*, 1904, ii., 129), that of quinaldine and its homologues (*Gazz. Chim. Ital.*, 1906, ii., 172), and, lastly, those observed by Benrath (*Phys. Chem. Centralblatt*, 1906, iii.), of the products which are formed by condensing benzoic aldehyde with quinaline, quinaldine, and cinnamic acid, from the last of which dibenzoyldiphenylbutane is formed.



(NOTE.—Stobbe refers to photosyntheses by Frankland and by Sernow, but I have not been able to find their papers. *Later addition.*—Frankland's experiments (*Ann. de Chim.*, 1851, lxxvii., 122) deal with the action of mercury on alkyl iodides, those of Sernow (*Bull.*, 1902, [3], xxvii., 14) with a similar behaviour of iodopropionic acid. Further, Duclaux states (*Ann. de l'Inst. Nat. Agronom.*, 1884-85, 286) that on exposing calcium lactate and mercury nitrate to light butyric acid is formed).

This, in a general way, is our knowledge about the action of light on organic substances and on the syntheses



which by its means it has been possible to realise. The greater part of the reactions that have been observed may be reduced to phenomena of reduction and of oxidation, which may be obtained by other means.

Not only therefore does the actual state of studies not allow the illusion of believing that chemistry has already entered the way which will bring us to explain the wonderful syntheses which take place in living plants, but, on the contrary, it makes us feel that to the present time the chemists have not drawn from such a powerful agent as solar light is, all the utility which doubtless it will be able to afford.

And since in the few instances, in which the transformations have been obtained with substances other than alcohols, the products of transformation have not been studied, nor has any knowledge been collected on the mechanism of the reactions, I have thought it might not be a useless task to undertake such a study.

I shall now occupy myself only with the researches made together with Dr. G. Chieffi on the behaviour of hydrocarbons with benzophenone, with some aldehydes, and with some other oxygenated substances which easily take hydrogen from them. The principal facts that we have hitherto ascertained are the following:—

1. Amylene (trimethylethylene) combines directly with ketones and with aromatic aldehydes, generating a series of compounds very important for both constitution and behaviour.

2. Paraffinic hydrocarbons are transformed into olefinic ones, which unite themselves with a part of the ketones to give compounds like the foregoing, or by direct combination give tertiary alcohols.

3. Aromatic hydrocarbons, according to the nature of the side-chain, react giving complex hydrocarbons, tertiary alcohols, and other substances.

4. Various organic substances, compound ethers, oxides of alcoholic radicals, &c., react, losing some hydrogen and forming unsaturated compounds which are added to the ketone, or they give directly addition products.

5. The products of addition of ketones with unsaturated hydrocarbons (aliphatic or aromatic), and with other unsaturated products derived from oxygenated substances have often the behaviour of resins or of natural balsams, having, nevertheless, a definite composition, molecular weight easily determinable, and a well ascertained chemical structure.

These results, as we shall better see afterwards, are not without importance, and they open a new and a large way to still more important researches; but unhappily, I say it again, it would be foolish to think that by them a decisive step is made towards the solution of the great problem of the organic synthesis which is accomplished in plants. To obtain such an aim it will be necessary before anything else to determine exactly what an influence light really has in the complex series of phenomena on which depends the elaboration of the immediate principles in plants.

Because, if it is proved that light is indispensable to the assimilation of carbon, it is also known that the decomposition of carbonic dioxide happens in the still living leaves, and on the other side it is known that in plants some principles are formed, and, among the others, all the colours of the flowers, for which if light is necessary, it is also an agent of alteration as soon as they are taken from the influence of vital functions, and other principles are formed which are, I should say, endowed with photophobic properties, because they collect and hide themselves in the parts less exposed to the light, or they impress on the plants themselves movements such that the least possible surface be exposed to the light.

Besides, we must always bear in mind that the conditions under which all photosyntheses have till now been accomplished, though distinguished from the other syntheses accomplished in the laboratories by the feature of the less elevated temperatures or because no recourse is had to gradual and successive processes in order to arrive at a

determined result, yet have nothing in common with the conditions that obtain in plants.

In plants all the reactions take place in the presence of water, while all the photosyntheses have been made without the intervention of this solvent. If in plants you take away the proteids, fats, oils, and carbohydrates, all the other substances that are elaborated are produced in a very small quantity in respect to the weight of the plant, and they are immediately eliminated or accumulated in determined organs; the greater part of the immediate principles of the plants represent, therefore, that which the secondary products represent in one of the common reactions of organic chemistry; while in the photochemical reactions the compounds till now examined are the principal products of the reaction.

In the plant too we have special conditions such as pressure, the action of the capillarity, the state, now of insolubility now of colloidal form, of the substances that react, the different permeability of the walls of the cells for the various products elaborated or in elaboration, the presence of numerous substances which act catalytically, and so on; all conditions which evidently must influence in some way the course of the reactions and which we are far from having attempted to reproduce in our photosynthesis.

It is not therefore a sign of discouragement if we are obliged to conclude that no portion has yet been raised of the thick veil that wraps round in the deepest mystery the mechanism of the marvellous process by which from two seeds, often so like in appearance and in composition, put in the same conditions quite different plants are formed, and in whose organs with unchangeable intercourse the most precious nourishments, the sweetest odours, the most salutary remedies, or the most terrible poisons, the most disgusting or stinking substances are elaborated and accumulated; for that does not signify that to the daring of human mind and to the patient work of the studious will be denied this triumph.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, April 22, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Deep Water Waves, Progressive or Stationary, to the Third Order of Approximation.*" By LORD RAYLEIGH, O.M., F.R.S.

The principles of hydrodynamics are applied to form the equations of wave-motion to the third order of approximation without restriction other than that the motion is irrotational and in two dimensions. The results are then applied to the progressive wave of permanent form, as investigated by Stokes, and to stationary waves. It appears that the form of the latter at the moment of greatest deviation from mean level is the same as that of the permanent progressive wave, but that the periods of vibration corresponding to the same wave-length are different.

"*Chemically Active Modification of Nitrogen, produced by the Electric Discharge.*" (VI.). By the Hon. R. J. STRUTT, F.R.S.

"*Difference between the Magnetic Diurnal Variations on Ordinary and Quiet Days at Kew Observatory.*" By Dr. C. CHREE, F.R.S.

The paper considers the difference between the diurnal variations of magnetic force at Kew Observatory on quiet days and ordinary days (*i.e.*, all days with the exception of those of large disturbance). The data employed are from the eleven years 1890 to 1900. Taking mean data

for the whole year, the difference in the horizontal plane may be regarded as consisting, to a first approximation, of a harmonic oscillation of twenty-four hour period along a direction inclined  $64^\circ$  east of north and of a regularly progressive non-cyclic change in a second direction which is perpendicular to the former. The result, while true of the days of the year as a whole, is only imperfectly exhibited in most individual months.

*"Effects of Different Gases on the Electron Emission from Glowing Solids."* By F. HORTON.

An investigation has been made of the ionisation produced by a glowing Nernst filament when used as a cathode in a discharge tube in the presence of various gases of different chemical affinities for the material of the filament. It has been found that the actual electron emission from the filament is independent of the nature of the surrounding gas, at least for the gases, air, nitrogen, oxygen, and hydrogen, for at low pressures the thermionic currents measured under similar conditions in these gases were practically the same. At higher pressures the thermionic currents differ considerably owing to the effect of ionisation by collisions being different in the different gases. The increase in the current due to ionisation by collisions in hydrogen is much greater than it is in air, oxygen, or nitrogen.

The experiments were repeated with a Nernst filament covered with lime, and it was similarly found that the electron emission from lime under these conditions was not increased by hydrogen, although earlier experiments have shown that lime heated on platinum gives a much larger electron emission in hydrogen than it does in air. This appears to be caused by the hydrogen increasing the emission from the platinum, an effect which has been shown by H. A. Wilson to be due to the absorption of hydrogen by the metal. Lime and the oxides of a Nernst filament do not absorb hydrogen, and the electron emission from these substances is therefore unaltered by the presence of this gas.

That the electron emission from an oxide cathode is the same in oxygen and in hydrogen, gases which have very different chemical affinities for the material of the cathode, is evidence against the theory which has lately been put forward, that the electron emission from a glowing solid is due to chemical action between the solid and the surrounding gas.

*"Heats of Dilution of Concentrated Solutions."* By W. S. TUCKER.

More detailed study of the variation of heat of dilution with concentration is here described than has hitherto been published. Dilution was performed by short steps by addition of water at air temperature. Specific heats of solutions were accurately obtained for various concentrations so that heats of dilution could be calculated for any mean concentration.

Solutions of hydrogen and lithium chlorides and sodium hydroxide give results which appear to show a linear relation with mass concentration, for the range over which heat of dilution has an appreciable magnitude.

Curves are shown which indicate that this heat of dilution, if that linear relation be accepted, will vanish at such concentration as will suggest the formation of some simple hydrate of the solute. Thus the straight line connecting heat of dilution and mass concentration for hydrochloric acid solutions will, if produced, cut the axis of concentration at  $\text{HCl} \cdot 15\text{H}_2\text{O}$ . Solutions of lithium chloride and sodium hydroxide similarly yield hydrates  $\text{LiCl} \cdot 8\text{H}_2\text{O}$  and  $\text{NaOH} \cdot 8\text{H}_2\text{O}$ .

Equations covering these results for the concentrated solutions are of the type—

$$\frac{dQ}{dN} = \frac{a}{N} - b,$$

and the total heat generated on dilution from  $N$  molecules of water to  $\infty$  is—

$$Q = a \log_e N - bN + c,$$

where  $a$ ,  $b$ , and  $c$  are constants.

The same type of equation applies well to Thomson's results for solutions of sulphuric, hydrobromic, nitric, and acetic acids, and reveals limiting hydrates  $\text{H}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  and  $2\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ . For nitric and hydrobromic acids there is no associated water.

Dunnington and Hoggard obtained results for ammonium nitrate solutions which can be expressed by a similar equation yielding a limiting hydrate  $\text{NH}_4\text{NO}_3 \cdot 24\text{H}_2\text{O}$ .

These simple relations do not apply to dilute solutions, and results obtained seem to show that the more dilute solutions are very complex, while those of concentration  $N < 10$  show the same characteristic simplicity for all the available solutions hitherto examined.

*"Origin of the '4686' Series."* By T. R. MERTON.

An attempt has been made to obtain some information as to the origin of the "4686" series by measurements of the relative breadths of the "4686" line and the helium lines, from which the relative masses of the atoms concerned can be calculated according to the relations which have been found by Lord Rayleigh, Michelson, Buisson, and Fabry, and others. The conclusion arrived at is that either the breadth of the "4686" line is controlled by circumstances at present unknown, or that the line originates from systems of subatomic mass.

## CHEMICAL SOCIETY.

*Annual General Meeting, March 25, 1915.*

Prof. W. H. PERKIN, LL.D., F.R.S., President,  
in the Chair.

A FULL report of the meeting will be found in the *Trans. Chem. Soc.*, p. 542 (April, 1915).

*Ordinary Meeting, April 22, 1915.*

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Messrs. Alec Alfred Beadle, John Jacob Beringer, Richard Arnold Seymour Jones (killed in action), Arthur Sheridan Lea, David Alexander Louis, John O'Sullivan, Sidney George Rawson, and Otto Nikolai Witt.

THE PRESIDENT announced that the Council have appointed the following Committees for the year 1915—1916:—

*Finance Committee*—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William A. Tilden, and the Officers.

*House Committee*—Messrs. Horace T. Brown, R. Messel, J. E. Reynolds, J. M. Thomson, Sir William A. Tilden, and the Officers.

*Library Committee*—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, R. Meldola, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

*Publication Committee*—Messrs. H. B. Baker, B. Dyer, J. N. Collie, F. G. Donnan, A. Harden, T. M. Lowry, F. L. Pyman, G. Senter, and the Officers.

*Research Fund Committee*—Messrs. W. R. Bousfield, Horace T. Brown, H. B. Dixon, Sir James J. Dobbie, F. G. Donnan, P. F. Frankland, W. H. Perkin, W. J. Pope, J. F. Thorpe, W. Palmer Wynne, and the Officers.

Certificates were read for the first time in favour of Messrs. George Roger Clemo, B.Sc., County School, Penzance; David Owen Davies, 4, Victoria Avenue; Penarth; Albert Richard Henschley, M.D., Crowborough, Sussex; Frank Jagger, 24 Wade Street, Halifax; Walter Ratledge Twigg, Beverley, Beech Hill, Luton.

The PRESIDENT announced that a Memorial on "The Position of Chemical Industries" had been forwarded to the Prime Minister with a request that the Government should receive a deputation from the Society.

According to a communication received from the Committee of the van't Hoff Memorial Fund, the amount available for distribution as grants in aid of research during 1916, is about £108. Application for grants should be made before November 1, 1915, and should be sent by registered post to "Het Bestuur de Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het 'van't Hoff-fonds' Trippenhuys, Kloveniersburgwal, te Amsterdam," with a detailed account of the manner in which the applicant proposes to spend the grant.

Papers embodying the results of the research carried out may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of the papers embodying the results of the research must be forwarded to the Committee.

The following papers were read:—

"A Method for Distinguishing Tautomeric from Polymorphic Substances." By NEVIL VINCENT SIDGWICK.

"Studies on the Walden Inversion. Part I. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid." By GEORGE SENTER and HARRY DUGALD KEITH DREW.

"Derivatives of 2-Pyridylhydrazine and 2-Quinolyldihydrazine." By ROBERT GEORGE FARGHER and REGINALD FURNESS.

"The Rate of Hydration of Camphoric Anhydride." By BERNARD HOWELL WILSDON and NEVIL VINCENT SIDGWICK.

#### ROYAL INSTITUTION. Annual Meeting, May 1, 1915.

Sir JAMES CRICHTON BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1914, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy-Faraday Research Laboratory Committee was read. Forty-four new Members were elected in 1914. Sixty-two Lectures and nineteen Evening Discourses were delivered in 1914. The books and pamphlets presented amounted to about 378 volumes, making with 652 volumes (including periodicals bound) purchased by the Managers, a total of 990 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

*President*—The Duke of Northumberland.

*Treasurer*—Sir James Crichton Browne.

*Secretary*—Col. Edmond H. Hills.

*Managers*—Sir Thomas Barlow, Bart.; Dr. Horace T. Brown; Dr. J. H. Balfour Browne; Dr. Andrew Carnegie; Charles Edward Groves; Sir Robert Hadfield; Charles Hawkesley; the Hon. Richard C. Parsons; Edward Pollock; Sir James Reid, Bart.; the Right Hon. Lord Rothschild; Alexander Siemens; Alan A. Campbell Swinton; Harold Swithinbank; the Right Hon. Lord Wrenbury.

*Visitors*—Rev. Edward S. Dewick; Lieut.-Col. Henry E. Gaultier; Joseph G. Gordon; Dr. William J. Gow; Dr. J. Dundas Grant; John W. Jarvis; James Y. Johnson; H. R. Kempe; Francis Legge; Francis K. McClean; Ernest R. Moon; Richard Pearce; Henry G. Plummer; Arthur J. Walter; Sir Henry J. Wood.

#### INSTITUTION OF CHEMICAL TECHNOLOGISTS. (LONDON SECTION).

Colonel CHARLES E. CASSAL, V.D., President of the Institution, in the Chair.

(Continued from p. 214).

MR. W. J. DIBDIN, F.I.C., F.C.S., Vice-President (Consulting Chemist, formerly Chief Chemist to the London County Council).—Mr. President, I was formerly chemist to the Metropolitan Board of Works and to the London County Council and for fifteen years I held that position. When I left it I left it a good going concern which was taken on by my successor who carried it on up to some two years ago, when he retired. I was going to refer to that in order to illustrate one of the most remarkable instances of the want of appreciation of chemical technology that has ever been known. I will mention this one fact, that the operations of the Chemical Department of the London County Council and the Metropolitan Board of Works effected a saving in one particular item of £10,000,000 capital expenditure to the ratepayers of London. It is a fact that if it had not been for the work successfully carried out by the chemical staff of the Board, London would have spent no less than £10,000,000 more than they did for the treatment of London sewage. The process was evolved out of the technical knowledge of the staff and of the chemical advisers, other than the staff, whom the Board wisely consulted, and the net result was that entirely new ideas were discovered and put into force, and London has had the benefit of that work, the process which was put into work twenty years ago being still at work and keeping the Thames free from nuisance. That one fact alone justified the existence of the Chemical Technological Department of the London County Council without saying one word about all the other technological work carried out by the staff. I am not speaking because I was one of that staff. There were one hundred of us altogether, all engaged in it, and that was the net outcome of our work in one direction alone. The reward of the chemical profession is this—the ratepayers of London have acknowledged the work done by its chemical technologists by abolishing the department. (Shame.) There is no chemical department of the London County Council. One part of the work is split up and put under the direction of a clerk—an admirable man, a most courteous and kindly man, but who had never seen one of the operations conducted for which he is now made responsible. That was one branch. The purely chemical work which was carried on was actually placed under the medical officer. He is not an analytical chemist and he cannot have that acquaintance with chemical technology which is necessary. The thirty-five Committees formerly made constant reference to the chemical technologist for advice, and now the whole of the thanks of London is expressed by the abolition of the Technological Department and by putting the chemist back into a position where he is a subordinate of the medical officer. I do not speak with reference to myself. It is nearly eighteen years ago since I left. All this has happened within eighteen months. It is a disgrace to London and to England and to the chemical profession that such a state of things has arisen. Whoever is responsible I hope it will be remembered against him, but the loss of incentive to the best work is such that it can only result in damage to the community. With regard to the position of the chemical technologist, the chemical technologist is to be compared with the foundation-stone of a building. He is there doing the work and the structure rests on him, but he is very seldom seen or heard of. I think the time will come when he will be unearthed and brought to light, and appear in his proper position. With regard to the status of the chemical technologist that is what I call the works chemist—the Institute of Chemistry is to blame, I think. Proposals have been taken up to enable students at our polytechnics who have given considerable promise to obtain a thorough grounding in

chemistry and to admit them to examinations. Now, says the Institute of Chemistry, if you have not paid the fees at a certain number of colleges we will not admit you; your ability may be great, but your father was not rich enough to pay the fees at certain colleges; it does not matter what work you can do or what contribution you can make to chemistry; you shall not come into our ranks because you have not attended certain colleges. I say that this is a great hardship and wrong to a large number of men whose parents are not in a financial position to pay the heavy fees, who are able to go to these polytechnics, and have acquired a sound knowledge of the work, but the Institute of Chemistry closes its doors and says, "Your father is a poor man; keep outside." That is one thing that the chemical technologist, the despised works chemist, feels keenly. That is the cry of these men, which has come up to some of us, and I have not been able to close my ears. I do sympathise with them. That is one reason why this Institution of Chemical Technologists has been formed. The Chemical Society is a most excellent Society, but it is of a totally different character. The Society of Chemical Industry is a manufacturers' society, but the Institution of Chemical Technologists brings together those engaged in the chemical works of the country—they are called works chemists, who feel as if they were treated as outsiders by the profession. Their position in the works may be seen from the disgraceful "salaries" paid, some of them receiving 30s. a week. How can men work at their best, how can their brains be at ease, when they are worried? The country must wake up to the appreciation of the work of those who have done so much and such good work in a quiet, unostentatious manner, and without whose work many industries would be nowhere. I say nowhere—they *could not exist*. I will give you one instance. Some years ago English cement manufacturers ruled the world. You could not get cement elsewhere. It was chiefly made on the Medway, but the German cement manufacturers entered into competition, and they said, "Why not make cement equal to the English?" What did they do? They went to Prof. Fresenius and said, "The English are making this cement. Can we not also do so?" Prof. Fresenius, a fine chemist, went into the question, and showed them on chemical lines where they were at fault, and the result was the Germans produced a better cement than the English manufacturers, and the latter were in danger of being driven out of the market by the imported German cement. They were woken up largely at the instance of John Grant, one of the assistant engineers to the Metropolitan Board, who went by the name of "Cement Grant." The English manufacturers woke up to the necessity of employing chemists in their works, and now there is hardly a cement works without their chemist. In a large number of cases the chemist's salary is something less than that of some of the workmen, but that industry would have gone over to the Germans if the English had not realised the fact that scientific works in the hands of the Germans would have ruined them, and they had to come to the chemist to be rescued from the position they had put themselves in. That is one instance. The question is not so much what is the cause of the condition of which many complain, but, I take it, the question is what can be done to remedy it? It is one thing to point out a defect and another to point out the remedy. There may be many suggestions, but I venture to think there is only one fundamental remedy. It is not by urging the Government to do this or that, or asking somebody else to do something, but it is for the chemical profession to rise up in its strength and say, "This state of things shall no longer be. We assert ourselves as valuable members of the community, and we will not be treated in the way we have been." It is a common observation that you can get a chemist and put him into a back room to make stinks to amuse himself, but the fact must be recognised that in modern industry the technical chemical adviser is one of the foundation stones of the concern, and he must be recognised and treated as such,

and not as an inferior—as one merely to be tolerated by the works foreman. That must stop. I say the country must wake up to the fact that the position of the chemist must be acknowledged and his responsibility recognised, and we must cease from placing him in the background as an inferior being and working him to death on starvation wages. I say this: I am sorry we have not here some more of the leaders of the chemical profession, who are too much self-centred in their own positions. (Hear, hear.) Many of them we admire and love as chemists, but they have not wakened to the position of their chemical brethren. I do hope that the time is not far distant when they will put themselves shoulder to shoulder, and that they will realise that they are members of an important portion of the community, and that on their shoulders rests a responsibility in proportion to their position. They must recognise that below them in the strata of life there are others working on the same lines, who have a right to look up to them for comfort and support in their strife and in their hardships. If their conduct is callous and self-sufficient monopolists will treat them as useful off-shoots of the industry and nothing more. This position must be altered. The chemical technologists, the works chemists, the falsely so-called lower ranks of the chemical profession, cry aloud to the officers of the army of chemistry to be led as they ought to be led, to receive every comfort which the man in the ranks has a right to receive from the knowledge that his commanding-officer is worthy of his trust. (Cheers.)

Mr. WILBERFORCE GREEN (Registrar).—Mr. President, we all agree that when the present war is over the commercial relations and the industries of this country will have undergone profound changes, and I assume that it is in anticipation of these changes we are met here to-night. I think this is mainly a subject for the chemical technologist—the scientific chemist. In spite of what is said or implied to the contrary, the chemical technologist is and must be ultimately responsible for the successful application of chemical principles to practical problems. Our main commercial rival has characteristics that we cannot disregard. We cannot overlook the power of organisation, the technical skill and co-operation, and other characteristics, which are not usually counted as virtues, to which reference has been made by some this evening. It is obvious that no military reverses can possibly destroy these characteristics of our foes, and these characteristics will be no less apparent when our rivals seek to regain the positions lost in the commercial world at the end of the war. We must prepare ourselves for what we have to face. Commercial organisation must be undertaken, and though to-night I am not concerned with this I cannot help observing, and in doing so I am paying the manufacturers back in their own coin, when I say that their house wants putting in order, that they might permanently extend and strengthen their trade if they would attend to those details of our commercial life. I am concerned here with the professional side of chemistry. I say that it is essential to our success that the chemical profession should be strengthened and consolidated. Chemical science is the basis of all modern industry, and neither engineers nor manufacturers can do without the powerful resources of the science, and the chief exponent of that science is the scientific chemist. Professional chemists should form a scientific army on which we can rely when steps have to be taken in any direction that is necessary. If we ask what we have done to form such an army, the answer is that we have done practically nothing in the last forty years; but if permanent success is to be attained—and I distinguish it from success that arises from exceptional and temporary conditions—means must be found to place the chemical profession in a position in which it may make its influence felt in every department of the manufacturing world. No serious attempt has hitherto ever been made to do such a thing. Years have passed. The importance of applied chemistry is unquestioned. Technical schools have been founded all over the country, and

he study of chemistry is regarded as a necessary part of education. In every university there are "chairs" of Chemistry and money is freely spent in training technical students. Time and money have been spent in technically training the individual, but not the slightest effort has been made to develop those attributes which give to the medical and legal professions their dignity, strength, and stability. There has not been a single attempt to develop a corporate professional life. That, I submit, is a fact of the very first importance. If I may take an instance from a military point of view, you can have an organisation in all parts of the country to teach the use of the rifle, and if men are keen on joining, you might have two hundred or three hundred thousand men, or many more, all learning to be in this respect individually efficient, but it would be absurd to say that under those conditions you had an army. Any man who believed that and acted on his belief would bring the country down badly. Such men must be trained to act together. That means the arousing of a corporate spirit. The men must have a belief in themselves as individuals and as members of a corporate body, and confidence in their leaders. I ask you to consider the history of the medical profession. One hundred years ago the medical profession was in the same position as the chemical profession is now. The work which resulted in the formation of the medical profession as we know it was initiated by the leaders of the profession, and the medical profession was thus built up. Those teachers had public spirit, a sense of duty towards and confidence in their profession, and their foresight and aptitude to lead made them to take up a strong, consistent, and definite line of policy, and to pursue it fearlessly to the end. These were the characteristics of the leaders of the medical profession. Their action resulted in the Medical Practitioners Act, 1858, being passed. That Act was not passed without strong opposition. The ignorance of lay reactionaries said that it was not for the medical profession to declare what should or what should not constitute a qualified man, but that is the objection which many put forward now in respect to the chemical profession. Fortunately for the medical profession those remarks passed unheeded. In the same year was passed the India Bill. The India Bill took the administrative control of India from the hands of those who were commercially interested in India. It was felt to be contrary to good principles of government that administrative interests should be subordinated to the commercial interests—in other words, it was an admission that the control of professional matters should be left in the hands of professional men. We can make no exception whatever in the case of the chemical profession. If it is sought to make the chemical profession an exception, it is a tacit admission on the part of those who are teaching that students are being trained in and for work of an inferior and unimportant kind. It is a tacit admission by those who are practising that the profession of which they are members is of so low an order that it is not worth governing as other professions are, and that this administrative work, which means so much, can be partly, or preferably wholly, left in the hands of those whose interest in it is merely secondary. The men who are responsible for the manufacture of armour-plate or explosives—is their work inferior? The work of the chemical profession cannot be said to be inferior to that of the medical or legal professions, nor do its aims and ideals fall short of the needs and aspirations of these times, but when we come to consider these ideals and the nature of the efforts made to attain these ideals, one realises how far short performance is from the ideal. The efforts made have been inadequate and weak, characterised by timidity of a most shameful kind, and exhibit a total lack of any appreciation of what a profession ought to be. If the chemical profession is to take its place among the great professions, its government must be left in the hands of professional men. The truth of that principle has been generally admitted. We desire to see the qualified chemical practitioner taking his place along with the doctor, the lawyer, the actuary,

and the accountant. The interests of the chemical profession must be furthered and controlled by its *real* representatives. We intend that the present disgraceful and humiliating state of things shall be put an end to, and that the youth shall not enter as a chemical student any more than he can as a medical student unless he realises what is expected of him by his profession, and what he may expect from his profession in return. The medical or law student knows what he has to do to qualify for his career. It is pointed out to him that he is a member of a corporate body; it is made clear to him that such a condition is for the good of all, severally and collectively. On the other hand, the profession "hall-marks" him and gives him a status; it undertakes to support his professional claims. That bargain reacts on the interests of the individual. We may regard his profession, run on such lines, as discharging a national duty. It has an ethical basis, apart from a purely technical one. When we come to the chemical profession we find no public spirit is inculcated in its members—that no attempt has ever been made in this direction. It seems to me that we have come to something which is in the nature of a "confidence trick." We have allowed money to be poured out like water. Technical schools have been run up, but no attempt has been made to lay down the details of a *minimum qualifying course*, to co-ordinate the work of the schools throughout the country, or to make students realise that there is a corporate life and corresponding obligations. You will search chemical literature in vain—in all the thousands of pages of printed matter you will search in vain—to discover one line in which encouragement is held out or advice given to chemical students. You will not find one address which is comparable to those most admirable addresses which are given in the medical schools at the opening of the session. Chemical students on leaving college find there is no professional body behind them, but that their profession *qua* profession is practically non-existent. There are no lists like the Medical Register, and no lists as in other professions. Nobody knows how many technical chemists there are in the country. I had occasion to communicate with the census authorities with regard to this matter. They do not officially know of the existence of the scientific chemist. Scientific chemists are lumped together with others under the heading of "People engaged in scientific occupations." The public generally confuses the technical chemist with the pharmacist and druggist, while the manufacturer calls himself a manufacturing chemist, although in the majority of cases he has no right to the latter part of the title.

This is the record of the chemical profession up to the present. There has not been a single corporate voice raised to protest against such a state of things; there have only been single voices crying in the desert. To gull a boy to believe he is going to enter a profession, of which the foundations have not been laid, is doing him a grievous wrong. It is on all fours with the action of the man who persuaded Martin Chuzzlewit to go to a place called "a city" which was found to be a swamp, and, said Mark Tapley, "an uncommon nasty one."

I would like to say one more word. We have heard about "silent pressure" in the North Sea. There is another kind of "silent pressure." It has come from Germany. It has been exercised steadily and stealthily for thirty years in a most effective way to our detriment. It is because our leaders in the chemical profession did not realise in the way our naval leaders realised what was due from them that that stealthy pressure has become as effective as it has. They have not inspired the rank and file of the profession with *esprit de corps* because they themselves have not been inspired with the recognition of public duty. If the chemical profession is to be developed the arousing of a professional spirit will be the determining factor in the process, and go far to determine the success of our struggle with Germany. If we neglect to do this we shall fail because we have not availed ourselves of that store of professional energy. This is the



ethical side of the question on which I wished to dwell, and I may say that though the commercial supremacy may seem to be the material one, in reality it is the ethical side that is going to count. It is first our duty to bring about a true professional feeling in the chemical profession. (Cheers.)

(To be continued).

## NOTICES OF BOOKS.

*Discussion of Evidence on the Solvate Theory of Solution obtained in the Laboratories of Johns Hopkins University.* By HARRY C. JONES.

THIS monograph, which is a reprint of Chapter VII. of Publication No. 210 of the Carnegie Institution of Washington, contains a brief discussion and summary of the more important lines of evidence which have been brought out by the work of the author and his collaborators on the solvate theory of solution. Beginning with the early research done under Arrhenius at Stockholm he reviews the experimental data accumulated, including the spectroscopic work, and shows how the results all point to the conclusion that when solution occurs there is always more or less combination between the dissolved salt or its ions and the solvent, the magnitude of the action depending upon the nature of the substances involved. It is shown that the solvate theory is not by any means to be regarded as a rival of the theory of electrolytic dissociation, but rather begins where the latter leaves off, explaining the condition of the ions after their formation. The two theories together constitute a comprehensive theory of solutions in general, not merely very dilute or "ideal solutions," and the monograph provides an excellent exposition of the main features of the theory of solvation.

*O Espelho.* ("The Mirror").

THIS is the only illustrated Portuguese periodical published in Great Britain and circulating in Brazil and Portugal, and it will undoubtedly do very valuable work in these two countries. Its aims are, firstly, to combat the German press campaign which is endeavouring to undermine British prestige, and, secondly, to develop commercial relations between Britain and Brazil, so that our merchants may have an opportunity of capturing Germany's South American trade. The type is good, the illustrations are excellent, and the *résumés* of European news are compiled from the most reliable sources. For the present the periodical is to appear fortnightly, and the production of a Spanish edition is contemplated. Efficient arrangements have been made for the distribution of the paper, which will undoubtedly be a very useful advertising medium for British firms.

## CORRESPONDENCE.

INSTITUTION OF CHEMICAL TECHNOLOGISTS.  
(LONDON SECTION).

*To the Editor of the Chemical News.*

SIR,—In your impression of April 23rd the President of this new "Institution," Colonel Cassal, endeavoured to unfold, as the subject for discussion on March 11th, "*The Future of British Chemical Industry.*" Among those "keenly interested in the subject" but prevented from attending, Mr. Bonar Law, Mr. Austen Chamberlain, the Earl of Denbigh, Lord Charles Beresford, and Captain Bathurst were named. As authorities on the subject of chemistry and its applications in chemical industry it is regrettable that these gentlemen were prevented. Had they been present a clear definition of what "technical chemistry" really is might have been called for, the study and practice of which is stated as being the object of the

new "Institution." It certainly receives no definition at the hands of Colonel Cassal. According to him, the Chemical Society of London is "entirely" concerned with theoretical chemistry, and he speaks of "applied and technical chemistry" as "*branches of science, i.e., distinct from each other.*" It would have been interesting to hear how and in what they differ. As to the "Society of Public Analysts" being restricted to the reading of papers on analytical subjects and the publication of a journal, it will be news to the said Society. A perusal of the journal of that Society leads me to note that discussions on the subjects of the papers form a very essential feature of its proceedings. With regard to the "Society of Chemical Industry" and its "main concern with chemical manufacture from the present unfortunately restricted point of view of the ordinary British manufacturer," I should, doubtless in common with many others of your readers, like to know what an "ordinary British chemical manufacturer" is, and how he differs from the "extraordinary" brand. We are told his powers of mental vision are "unfortunately restricted," and it is only such short-sighted or semi-blind people that "the Society of Chemical Industry is mainly concerned with." The Society issues an alphabetical list of members. Perhaps Colonel Cassal will kindly give a few typical and prominent names of ordinary manufacturers with such restricted vision, and opposite to them a few of his ideal men with practically unlimited vision. It is clear from his acknowledgment that the Society of Chemical Industry by publishing its journal and in other ways "has done excellent work," that he merely refers to a kind of pioneering, or leading gently upwards to a higher platform, which through lack of further mental calibre it must resign in favour of the "Institution of Chemical Technologists"! As indicative, I presume, of restricted visionary powers, Colonel Cassal mentions that "unfortunately the membership is not confined to professional chemists." Let us ask his definition of "professional chemists," and further let us ask, why is it "unfortunate" to seek to extend knowledge, whether of chemistry or any other subject? Also, why is it "still more unfortunate" to extend the benefits of the Society and its journal beyond the seas and to other lands? Have we in Britain the entire monopoly of chemical technology? May we humbly crave the names of at least a few of those "qualified to judge" that such extension is highly dangerous, and even "probably extremely injurious to the interests of British chemical industry?" Of course, had the Society of Chemical Industry only possessed the far-sightedness or gumption referred to by Colonel Cassal, and attempted to confine the limits of its fold first to professional chemists and second to British subjects, there would, now that his Institution of Chemical Technologists has started, have indeed been "a great many professional chemists actively engaged in most important work," &c., &c., to collect for his Institute—a perfect harvest in fact! From what he says, it will now be "the business" of the new Institution "to collect the isolated and unquestionably valuable elements and to put them in their proper places in an organised body." Personally, were I one of these so called "isolated and unquestionably valuable elements," I should feel the reference addressed to me as one of a body that needed apologising for, a chemical wanderer on the face of the earth, but still one that might be "organised"—whatever that may mean. I can readily imagine the reply of the professor of "pure chemistry" to a further statement of Colonel Cassal's, as to there being at present no relationship or sympathy between the college laboratory and the technical laboratory, which the new "Institution of Chemical Technologists" is to rectify, and it is briefly this: "The student of chemistry is in the college and the college laboratory to learn chemistry, so that he may eventually be possessed of the wherewith-all—to apply!" If he tries to do both together, and within the same college period, and college laboratories generally fall in with Colonel Cassal's scheme, then indeed that "broadly-

based Institution, free from the trammels of older bodies, constituted for the needs of to-day," will find a rich harvest of benighted wanderers; but to put them in their proper places in an organised body involves a further question, viz., Where is their bread and cheese to come from? I should rather fear that for not a few of them the broadly-based institution will turn out to be no other than—the workhouse!—I am, &c.,

WATSON SMITH.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx. No. 11, March 15, 1915.

This number contains no chemical matter.

No. 12, March 22, 1915.

**Crystalline Theobrominate of Calcium.**—Louis Rousseau.—When a molecule of lime acts on two molecules of crystallised theobromine in presence of water freed from carbon dioxide, the two substances combine on boiling, and when cooled a crystalline mass is obtained. When kept over sulphuric acid the composition of the substance corresponds to the formula  $(C_7H_7N_4O_2)_2Ca \cdot 9H_2O$ . It slowly loses its water of crystallisation at about 120°. It does not dissociate in water, and is only very slightly soluble in alcohol. Carbon dioxide reacts with it, regenerating theobromine and forming calcium carbonate.

*Bulletin de la Société Chimique de France.*

Vol. xvii.-xviii., No. 1, 1915.

**A Variety of Selenium Particularly Sensitive to Light.**—Louis Ancel.—When vitreous selenium is fused at 220°, and rapidly cooled under pressure, it is transformed into a new grey variety, which is very sensitive from a photo-electric point of view, but is very unstable. In order to employ this variety it must be mixed with a small quantity of vitreous selenium, and the combined action of heat and pressure will produce a sort of solid solution, which is quite stable, of the grey in the vitreous variety. The great sensibility of this selenium is only apparent when the layer of the non-metal is formed on a metallic electrode, a selenide being probably obtained. Copper is a suitable metal to use for the electrodes.

**Use of Nickel and its Oxides in Catalysis.**—J. B. Senderens and Jean Aboulenc.—Metallic nickel when finely divided is a hydrogenating catalyst, equally suitable for use in the wet and dry ways. The oxides of nickel seem to be inactive for hydrogenations in the dry way. When used in the wet way they appear to have an activity of their own which cannot be ascribed to the presence of reduced nickel, and they behave like catalysts whatever the degree of their oxidation.

## MISCELLANEOUS.

**Royal Institution.**—A General Meeting of the Members of the Royal Institution was held on the 3rd inst., His Grace the Duke of Northumberland, K.G., President, in the Chair. Mr. Richard H. Beamish, Mr. William E. Benton, and Mr. Charles A. Schunck were elected Members. The Special Thanks of the Members were returned to Dr. Thomas W. Dewar for his Donation of £15 15s. to the Fund for the Promotion of Experimental

Research at Low Temperatures. His Grace the President announced that he had nominated the following as Vice-Presidents for the ensuing year:—Sir Thomas Barlow, Bart., Dr. J. H. Balfour Browne, Charles Hawkesley, Edward Pollock, Sir James Reid, Bart., The Right Hon. Lord Wrenbury, Sir James Crichton Browne, Treasurer, Colonel Edmond H. Hills, Secretary.

**Institute of Chemistry.**—*Pass List: April (1915) Examinations.*—Of five candidates who presented themselves for the Intermediate Examination, two passed:—T. L. McEwan, B.Sc. (St. Andrews), and E. Mendoza. Of ten candidates who presented themselves for the Final (A.I.C.) Examination, eight passed:—In the Branch of Physical Chemistry—E. K. Rideal, B.A. (Cantab), Ph.D. (Bonn). In the Branch of Organic Chemistry—W. S. Allen and Gilbert Harding. In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers, and Feeding Stuffs, Soils, and Water—A. S. Carlos, B.Sc. (Lond.); R. H. Hopkins, B.Sc. (Birm.); D. A. Legg; A. R. Pearson, B.Sc., A.R.C.S. (Lond.); and G. A. Stokes.

**Institute of Metals Corrosion Committee.**—In the absence, on active service, of Dr. G. D. Bengough, M.A., Honorary Investigator to the Corrosion Committee, now a Captain in the Royal Garrison Artillery, the Council of the Institute of Metals have appointed Mr. W. E. Gibbs, M.Sc., as Acting Honorary Investigator to the Committee. Mr. Gibbs, prior to the outbreak of the war, was acting as Dr. Bengough's assistant in connection with the work for the Corrosion Committee. He is now engaged on a series of important investigations, the results of which will be embodied in the Third Report to the Corrosion Committee, which it is hoped will be presented at the forthcoming Autumn Meeting of the Institute of Metals.

**Proposed Trade Conference at Swansea.**—The Swansea Corporation, Parliamentary, and General Purposes Committee on Friday (April 30) considered a letter from Mr. Gwilym Morgan, an ex-member of the Council, calling the attention of the Mayor to the recent Trade Conference at Cardiff, and suggesting that Swansea should arrange a similar conference. It was, he said, a matter of vast importance to Swansea which was such a centre for the production of metals and chemical compounds. "Unless you do something," said the letter, "Cardiff will take advantage of any concession that may come along and will not consider us." He mentioned the opinion of Principal Griffiths that Swansea should have one of the foremost technical colleges in this country, and that a Chair of Mining and Engineering ought to be established there. It was agreed to appoint a small Sub-committee to act with the Mayor in the matter.

## MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Royal Society of Arts, 8. (Cantor Lecture). "Food-stuffs," by David Sommerville, B.A., M.D.  
TUESDAY, 11th.—Royal Institution, 3. "The Animal Spirits," by Prof. C. S. Sherrington, F.R.S.  
WEDNESDAY, 12th.—Royal Society of Arts, 8. "Recent Progress in Pyrometry," by C. R. Darling.  
THURSDAY, 13th.—Royal Institution, 3. "The Movements and Activities of Plants," by Prof. V. H. Blackman, F.R.S.  
— Royal Society of Arts, 4.30. "Indian Trade and the War," by Sir Charles H. Armstrong.  
— Royal Society. "Development of the Thymus, Epithelial Bodies, and Thyroid in the Vulpine Phalanger (*Trachisaurus vulpecula*)," by Elizabeth A. Fraser and J. P. Hill. "Observations on the Development of the Thymus, Epithelial Bodies, and Thyroid in Phascogaster, Phascoglossus, and Perameles," by Elizabeth A. Fraser. "Measurement of the Specific Heat of Steam at Atmospheric Pressure and 104.5° C.," by J. H. Brinkworth. "Thermal Properties of Carbonic Acid at Low Temperatures," by C. F. Jenkin and D. R. Pyle.  
FRIDAY, 14th.—Royal Institution, 9. "The Archives of Westminster Abbey," by The Rev. E. H. Pearce, M.A.  
SATURDAY, 15th.—Royal Institution, 3. "Advances in the Study of Radio-active Bodies," by Prof. F. Soddy, F.R.S.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2894.

## MENTHOL : ITS MELTING- AND SOLIDIFYING- POINT.

By ROBERT MELDRUM

MENTHOL is stated by the following authorities to have melting-points as follows:—36° C., Oppenheim, Allen; 42° C., Beckett, Wright, Atkinson, Yoshida, Goodchild. Allen states the melting-point of pure menthol to be 36° C., and the commercial to vary between 41° and 43° C. The writer has undertaken the following investigation to ascertain the extent of variation in the melting- and solidifying-point of menthol by various methods and the causes of such variation. The menthol used was ordinary pure, the same sample being used throughout the experiments. The test-tube used for solidifying was  $\frac{1}{8}$  in. inside bore, unless otherwise stated. The thermometer was a 52° C., divided into tenths. The same thermometer and tube was used throughout the whole series of tests. When abnormal results were obtained the thermometer was tested against a standard one, but in each case no variation in readings was obtained. During the readings the thermometer was fixed in centre of tube about 1 cm. from bottom, the tube being half full of menthol.

METHOD A.—*Constant stirring in air at 60° F.*—Melted at various temperatures from 45° to 55° C. till all traces melted, and stirred with thermometer till temperature ceases to fall and thickening commences; fixed thermometer, and noted readings:—

Solidifying-point + rise, °C.	38·7	38·4	38·5	38·6	38·4
Rise, °C.	1·0	2·9	3·5	3·1	2·9
Solidifying-point + rise, °C.	38·2	38·5	38·1	39·1	39·0
Rise, °C.	1·2	1·7	2·6	1·6	1·8

Variation, 1·0° C. Minutes to rise, 10.

On stirring to cool a small portion of the menthol sets on bottom of tube, and nature of solidification depends on whether this is disturbed by the stirring and mixed up with the liquid menthol. If undisturbed the menthol at the supercooled temperature solidifies rapidly from top about half way down tube, and becomes so rigid that stirring cannot be continued, and thermometer has to be fixed in partly solidified and fluid. On the other hand, if menthol at bottom is disturbed by stirring solidification commences from bottom, leaving the upper part of tube fluid at commencement of rise. Due to the solidification becoming so rapidly rigid it is not possible to produce a homogeneous mixture of fluid and solid throughout the tube, and this no doubt is the explanation of the variation in results.

The solidification of menthol commences as a transparent colloid which rapidly becomes more opaque and more rigid. The longer the stirring is continued the higher the results; if the thermometer is fixed just as solidification commences low readings are obtained. Therefore uniformity in solidification depends upon an equal number of crystallising points being dispersed throughout the mass in unit of time, which fails to take place due to difficulty in stirring. The rapid increase in viscosity at the supercooled temperatures is no doubt due to menthol attaining the colloidal condition previous to crystallising, as the very slow rise points to this fact. The behaviour of menthol in solidifying is totally different from thymol, but approaches closely mutton tallow and the solid fats.

METHOD B.—*Stirred while being cooled in cold water.*—Melted at 50° C. and cooled by stirring in air to 40° C., plunged tube into cold water at 10° C., and continued stirring till temperature ceased to fall and thickening commenced, and fixed thermometer:—

Solidifying-point + rise, °C.	37·5	37·4	38·0	38·2	36·7
Rise, °C.	1·5	1·4	1·5	1·7	0·7

Variation, 1·3° C.

At 36° C. becomes so thick can hardly be stirred. At about 36° a layer of solid menthol forms round tube, the whole tube becoming rapidly solid. Time cooling and rising, two minutes. Degree of stirring, rapidity of cooling, and rapid solidification accounts for low results and variations. Here, also, a thick gelatinous mass forms at the commencement of the rise, Menthol is more erratic in its behaviour than thymol under this method. Thymol is fairly normal under the method.

METHOD C.—*Solidification while partially melted.*—Melted at 42° C. till three-fourths melted, and stirred in air jacket till thickening commences, and fixed thermometer.

Solidifying-point + rise, °C.	39·5	39·8	38·7	40·2	39·4
Rise, °C.	0·1	0·4	0·7	0	0
Solidifying-point + rise, °C.	39·8	41·3	41·4	41·4	40·4
Rise, °C.	0·1	0	0·4	0·4	0·4

Variation, 2·7°.

Solidification commences as a transparent colloid which rapidly becomes more opaque and rigid. Remains at maximum temperature for about three minutes.

It is not possible to attain a uniform mixture of solid and liquid menthol by stirring as the thickening approaches. The high results are due to stirring effects as the stirring here was continued beyond usual. Though solidification has taken place with no or little supercooling and in the presence of solid matter, it is seen how variable the results are. During the experiments it was observed that the solidifying-point varies according to the extent the solid menthol has been uniformly dispersed through the mass and the amount of solid present. There is no doubt that the colloid condition or thickening while transparent can be produced at high temperatures if sufficient solid matter is present.

METHOD D.—*Cooled by stirring in hot water jacket.*—

Solidifying-point + rise, °C.	39·5	39·8	40·3	40·2	40·4
Rise, °C.	0·3	0·6	1·1	0·5	0·9

Variation, 0·9° C.

Cooled by stirring in air to 42° and placed in hot water jacket at 42°, and allowed to cool at rate of cooling of jacket. Stirred menthol all the time, also water in jacket. At 39° C. becomes thick but transparent. The longer stirring is continued after thickening takes place the higher the rise. When semi-solidification begins, if thermometer is fixed, low solidifying-points result; if the stirring be continued till quite solid, or nearly so, high readings result. Therefore the results obtained depend on activity of stirring and its duration. To obtain a maximum rise and higher solidifying-point stirring is necessary while almost solid. When the thermometer registers highest temperature and ceases to rise, on disturbing the instrument a further rise takes place, thus:—

Thermometer ceases to rise at °C.	39·7	40·1	40·0
Disturbing thermometer rises to °C.	40·9	40·9	41·1

This behaviour of menthol under these conditions appears to be common to all solidifications below 40° C., whether in hot water jacket or not, and appears to indicate the importance of stirring or disturbance of the semi-solidified menthols to obtain high solidifying-points, due to final stages of crystallisation being hastened or completed.

METHOD E.—*Cooled in cold water without stirring.*—Melted at 45° C., fixed thermometer in centre, and plunged into cold water at 10° C. What takes place here is a rapid and gradual fall to 25° C., but no zero point, rise, or stationary point was observed. Solidification takes place from bottom of tube and extends all round sides which increases in thickness as the cooling proceeds

Cooling here takes place at greater rate than crystallising rate. The most interesting point of this experiment is failure to exhibit a definite solidifying-point, whereas by Method B, which is the same test but with stirring, a well defined though erratic solidifying-point is registered. We here see that rapid cooling and rapid solidification or thickening is apparently not sufficient to produce a stationary point, and that stirring, agitation, or disturbance of the solidifying or solidified mass seems to be necessary to yield a well defined solidifying-point. However, the results obtained by Method F, where slow cooling and *no stirring* is used, clearly shows that well defined, though somewhat low, solidifying-points are obtained. Therefore elimination of the three points is not due to lack of stirring but to rate of cooling being greater than crystallising rate.

**METHOD F.**—*Air cooled without stirring.*—Melted at 45° C., and stirred to cool to 41° C., fixed thermometer, and placed in apparatus to cool.

Solidifying-point + rise, °C.	37.5	37.6	37.4	37.7	37.3
Rise, °C. . . . .	2.8	3.0	3.4	2.9	3.0

Variation, 0.3° C. Minutes to rise, 20.

Minutes stationary, 0.5.

Solidification proceeds from bottom at first and progresses upwards, and then commences from top and on sides; therefore cooling and solidification is taking place at different parts of the menthol at different temperatures and different speeds. Though the results agree within themselves by 0.3° C. and are fairly constant, yet the solidifying-point indicated is below normal. This is but one instance of how false solidifying points result.

**METHOD G.**—*Supercooled in air and stirred.*—Melted at 45° C. and stirred to cool exactly to 43° C.; fixed thermometer and allowed to supercool to the indicated temperatures, stirred till thermometer begins to rise, fixed same and noted readings:—

Supercooled to °C. . . .	35	36	37	38	39
On stirring ther. falls, °C.	34.8	35	36	37	37
Solidifying-point + rise, °C.	38.2	38.2	38.5	38.8	38.9
Rise, °C. . . . .	3.4	3.2	2.5	1.8	1.9

Variation, 0.7° C.

Here also the indicated solidifying-point depends upon the degree and duration of stirring. After rise is complete at 38.2°, on revolving thermometer standing in solid menthol it rises to 38.9°; again, when solidification is complete at 38.9°, on revolving thermometer it rises to 40.3°. On re-melting the solidified core of menthol it is seen to be full of large cavities, no doubt containing fluid menthol. This would explain further rise on disturbing thermometer. That the further rise is due to friction developed by rotation of thermometer cannot be accepted, as thermometer does not rise when rotated at high temperatures—that is, at 40° C.

**METHOD H.**—*Adding menthol crystals to melted.*—Melted at 45° C. and cooled by stirring in air to 41° C., and added to per cent menthol crystals and continued stirring till thickening ensues; fixed thermometer for readings:—

Solidifying point + rise, °C.	39.0	39.2	39.8	39.7	39.5
Rise, °C. . . . .	0.8	0.4	0.6	0.5	0.4

Variation, 0.8° C.

After solidification complete, on revolving thermometer temperatures rise to:—

39.9	39.8	40.4	40.5	40.2
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Generally, a great deal of reliance is placed upon this method, as it is considered reliable and as yielding constant results. It will be seen the variation amounts to 0.8° C., and yields results which depend not upon the presence of menthol crystals but upon the activity and duration of stirring. Attempts were made to time the stirring in seconds, but this had to be given up, due to erratic thickening.

#### Solidification in Capillary Tubes.

In capillary tubes of 1 mm. bore menthol could not be maintained in the fluid condition at ordinary temperatures for more than fifteen minutes without solidification taking place. In these fine-bore tubes menthol solidifies to a transparent solid previous to crystallisation taking place. When the tube is half full of liquid menthol it may be moved up and down the tube, and as cooling proceeds, and when it ceases to move, a needle passed down tube, it is found to be quite rigid and hard. In this state it is free from traces of crystallisation, but crystallising points soon appear, and after twenty minutes gradually turns opaque. The importance of this fact in solidification phenomena cannot be over-estimated, as there is no doubt that erratic solidification of many substances is closely related to it. It is therefore evident that rapid change of viscosity at the solidifying-point, due to assuming colloidal conditions, are disturbing elements in determining the solidifying-point.

Menthol behaves like thymol when allowed to solidify on thermometer bulb. A thermometer immersed in melted menthol, withdrawn and allowed to cool, solidification only takes place at 15° C. on bulb; lower temperatures than this can be obtained by cooling the thermometer quicker.

#### Melting-point of Menthol.

**Thermometer Bulb Method.**—This method yields very constant results, as will be seen from results. Rate of heating about four minutes per degree:—

Large drop appears, °C.	42	41.9	42.0	41.9	42.0	42.0
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These figures agree with other observers, that the true melting-point of menthol is 42° C.

**Opacity Method.** Melting in test-tube  $\frac{3}{8}$ " diameter in large water jacket. Raising temperature jacket at four minutes per degree; stirring jacket and menthol during the test. Menthol 40° C., jacket 40° C., for five minutes. All solid round sides, semi solid in centre; does not drop from thermometer bulb. Menthol 40.5° C., jacket 40.5° C., five minutes; contents of tube in form of solid paste; does not drop from bulb. Menthol 41° C., jacket 41° C., five minutes; thick solid paste; does not drop from bulb; difficult to stir. Menthol 41.5° C., jacket 41.5° C., five minutes; very opaque paste liquid; drips from bulb. Menthol 42° C., jacket 42° C., five minutes; thin opaque liquid, not all clear. At 42.5° C. all traces melted and clear.

Three experiments gave the same results. This method, therefore, yields results half a degree higher than thermometer bulb method.

**Floating on Water Method.**—Placed 1 grm. in 200 cc. water and heated gradually; stirred water slowly. It melts at 39° C., but the actual point is somewhat indefinite.

**Menthol with 2 per cent Water.**—The water does not dissolve in the menthol but collects at bottom of tube as large globule, and increases in size as melting is prolonged. It would thus appear that water at the melting-point of menthol dissolves a considerable proportion, or that the menthol forms a hydrate which is only partly soluble in menthol:—

Solidifying-point + rise, °C.	31.3	31.2	31.0	31.5
Rise, °C. . . . .	2.3	1.7	0.2	1.5

Melting-point, 35° C.

#### Menthol and Oil of Peppermint.

Menthol 80 per cent + oil of peppermint 20 per cent.

##### Solidifying-point, Method A.—

Solidifying-point + rise, °C.	28.8	29.2	29.3	29.5
Rise, °C. . . . .	3.8	1.2	0.3	1.5

##### Solidifying-point, Method C.—

Solidifying-point + rise, °C.	30.9	31.4	31.8	30.7
Rise, °C. . . . .	0.0	0.6	0.8	0.2

Solidifying-point, Method G.—

Supercooled to °C. . . . .	26	27	28	29	30
On stirring therm. falls °C. .	26	26.5	27	27.7	27
Solidifying-point + rise, °C. .	28.7	28.8	28.8	28.8	28.7
Rise, °C. . . . .	2.7	2.3	1.8	1.1	1.7

In all these tests the colloid condition was assumed previous to crystallisation, and in solidifying the mixture behaves very like menthol itself. In hot water jacket the mixture solidifies at 32.8, 32.4, the rise varying from 0.2 to 0.4° C. When allowed to solidify in hot water jacket at rate of cooling of jacket, and allowed to cool down to 15° C. for twenty-four hours, the mixture is almost transparent, with little or no crystalline structure. At 15° C. no oil separates from the mixture, a homogeneous mixture of liquid and solid resulting. It will be seen, 20 per cent. oil lowers the solidifying-point about 10° C., or about the same ratio as thymol and oil of thyme.

*Melting-point of Menthol and Oil of Peppermint Mixture.*—By the thermometer bulb method varies between 33 to 34.5° C. six determinations. The melting-point of mixture by this method is therefore more erratic than menthol. By the opacity method constant melting-point is given of 34.5° C.

Summary.

Menthol solidifies below its normal solidifying-point, due to assuming the colloidal condition previous to crystallising. The solidifying-point varies as the colloidal condition varies. Its melting-point is constant at 42° C., but solidifying-point varies by 3.3° C. when determined by good methods.

PHOTOSYNTHESIS IN ORGANIC CHEMISTRY.\*

INTRODUCTION AND GENERAL CONSIDERATIONS.

By E. PATERNO.

(Continued from p. 221.)

NOTE XI.—General Considerations.†

OUR researches on synthesis in organic chemistry by means of light have been published from October, 1908, onwards in the *Gazzetta Chimica Italiana*. They, with the present one, constitute altogether eleven papers, nine of which are experimental, and made with the collaboration of Dr. Generoso Chieffi, and with that of Drs. Maselli, Traetta-Mosca, Forli-Forti, G. Perret, and R. De-Fazi. Besides those in Note I. the principal results obtained, and more precisely the reactions of a general nature that we have observed, were made known to the Royal Lincei Academy in the sitting of January 7, 1909. The papers following therefore represent but the experimental proof of what had been already stated. And if the publication of this material has been protracted for a period of about six years, that must be attributed to the numerous occupations which interfered with the work of compiling, and besides to the wish of extending to a greater number of compounds the reactions observed.

By reading the Introduction it is easy to every one to form an idea of our contribution to the problem of synthesis in organic chemistry by means of light, a problem which we have circumscribed to the application of light in the common work of synthesis in the laboratories. In the above named Introduction we have with the most scrupulous care, fixed the state of the problem towards the end of 1908, showing that only some isolated facts were then known about synthesis, and that the most complete and systematical work on the action of light, without the intervention of other catalysing agents, on the organic compounds was that of Ciamician and Silber

(*Gazz. Chim. Ital.*, xxix., [1], 237) begun in 1901, and chiefly directed to investigating the reducing action of alcohols on the quinones and ketones and nitro-compounds.

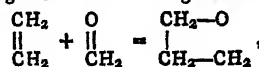
If afterwards some analogy could be traced between our researches and those of Ciamician and Silber, who for several years had passed to studies on hydrolysis, whoever will look carefully into the whole matter will not fail to observe that it is due to the fact that when these authors have known our results they have completed with success the study of some reactions, which at first they had occupied themselves with only because they were accompanied by a reducing action, but had stopped at the first difficulties which a more complete study offered.

I.

One of the most important reactions that we have observed and of which no previous example is known to us, is that which takes place by the action of light between the carbonylic compounds, aldehydes, and ketones, and the olefinic hydrocarbons. What takes place is the opening of the double link, and the direct addition between carbon and carbon, as is shown by the fact that from the products of the reaction we can separate some hydrocarbons that contain a number of atoms of carbon equal to the sum of those contained in the original substances. Thus from the product of addition of benzaldehyde,  $C_7H_6O$ , with the amylene,  $C_5H_{10}$ , we obtain the hydrocarbon  $C_{12}H_{18}$ , and from the product of the addition of the benzophenone,  $C_{13}H_{10}O$ , with the amylene the hydrocarbon  $C_{18}H_{22}$ .

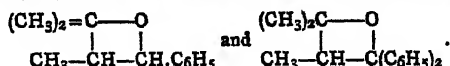
As to the constitution of the new compounds we would not say that it is perfectly cleared up; but we have fixed on a hypothesis that presents, without doubt, a great degree of probability.

The simplest representatives of the products to which this reaction is referred are evidently ethylene and formic aldehyde. Now nothing is more logical (we have not made the experiment) than that these two compounds can unite themselves together in the following manner:—



with the formation of trimethylene oxide.

From this scheme it is easy to deduct the reaction that ought to take place between the homologues of ethylene and formic aldehyde, or the ketones which are only alkylic derivatives of formic aldehyde. And therefore the compounds that are generated are only products of substitution of trimethylene oxide. With amylene (trimethylethylene) and benzoic aldehyde (phenylformic aldehyde) we must then obtain trimethyl-phenylethylene oxide, and with amylene and benzoketone (diphenylformic aldehyde) trimethyldiphenyl-trimethylene oxide, that is the compounds:



This reaction has the character of a general reaction, although, like all other general reactions of organic chemistry, may come about more easily with some terms of the series and less easily with others, and altogether fail in some cases.

As far as the aldehydes are concerned, the reaction has given us the best results with benzoic, anisic, and paratoluic aldehydes (*Gazz. Chim. Ital.*, xxxix., [1], 347, 347; xlv., [1], 154).

Negative results have been obtained with salicylic aldehyde, probably owing to the presence of phenolic oxyhydri (*Ibid.*, xlv., [1], 157). Of the fatty aldehydes we have only tried valeric aldehyde, with a result that seems positive (*Ibid.*, xxxix., [1], 347).

In this reaction it is to be observed that light polymerises amylene, whence the reaction cannot take place whenever for its accomplishment more time is wanted than that which is required for the polymerisation of amylene.

\* From the *Gazzetta Chimica Italiana*, 1909-1914.

† For the Papers II. to X., in which the experimental researches are exposed, see the *Gazzetta Chimica Italiana*, as quoted in the present paper.



With the ketones a typical reaction takes place with benzophenone and with acetophenone (*Ibid.*, xxxix., [1], 353); but also with benzylideneketone (*Ibid.*, xxxix., [1], 554), with benzoylketone (*Ibid.*, xxxix., [1], 354), with acetylhexamethylketone (*Ibid.*, xxxix., [1], 354), and with benzil (*Ibid.*, xlv., [1], 158) we have obtained encouraging results. Negative results have been obtained with ordinary acetone and amylene. Of other olefinic hydrocarbons we have experimented with caprylene (*Ibid.*, xxxix., [1], 355), hexylene, and hexadecylene, obtaining the best results with caprylene and benzoic aldehyde.

We wished further to determine whether other oxygenated compounds, differing in nature from aldehydes or ketones, were able to react with amylene. Our experiments, all with a negative result, dealt with benzyl and ethyl alcohols, with acetic, trichloroacetic, and oxalic acids, with dimethylpyrone, with xanthone, with saligenin (*Ibid.*, xxxix., [1], 356; xlv., [1], 158, 159, 160, 162, 257). We have also made experiments with acetonitril and benzonitril, as well as with aromatic hydrocarbons, viz., benzene and naphthalene, but in no case does any reaction take place.

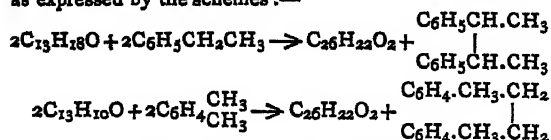
This condensation, which we shall call trimethylenic, takes place, then, exclusively with the ketones and aldehydes.

## II.

Another reaction of a notable importance we have observed between ketones and aromatic hydrocarbons. That hydrocarbons and other organic substances may act as reducing agents under the influence of light is a fact known for very long time, but in the case of hydrocarbons nobody had ever examined the transformation that they themselves have undergone.

In the year 1883 Klinger had already noted that, from benzil and phenanthraquinone with ether, aldehyde is formed, which he attributed to the alcohol which is formed by the hydrolysis of the moist ether, and Ciamician in the year 1886, as if to confirm it, observed that the transformation of alcohol into aldehyde takes place with quinone. But Ciamician and Silber, who with many experiments studied the reduction of quinones and ketones with various alcohols, revealing with care the products of an aldehydic nature which are then formed, when they have to do with the action of trimethylcarbinol, say (*Ibid.*, xxxii., [1], 222; *Rendiconti R. Accad. dei Lincei*, 1901, i., 93):—"In this case one would think that, the alcohol being a tertiary, no action takes place," and, after having said that the reduction has taken place, "what may be the transformation undergone by the tertiary alcohol we have not been able to discover."

And further on, occupying themselves with the behaviour of quinone with oxyacids, with acids, and with hydrocarbons, they never succeeded in determining what is the chemical action, nor had they better results repeating the reductions with ether, as Klinger had done. But more than this, Ciamician and Silber, in their Note V. to the Lincei Academy (*Gazz. Chim. Ital.*, 1904, i., 135; *Rendiconti R. Accademia dei Lincei*, 1903, i., 238), trying to elucidate the reduction of benzophenone with hydrocarbons, chose cymene with the hope of being able in this case to discover eventually also the transformation suffered by the hydrocarbon; but they did not succeed. In our researches the process has been explained. And, first of all, in the reaction between benzophenone and ethylbenzene and *p*-xylene we have shown that diphenylbutane and *p*-dixylol are formed; that is the reduction is as expressed by the schemes:—



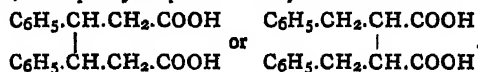
And this result we announced to the Lincei Academy in the aforesaid meeting of February 7, 1909.

It is indeed true that fifteen months and a-half later

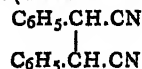
Ciamician and Silber made known the results of experiments begun several years before and then taken up again, adding new examples to the reaction that we had obtained, and showing that the re-doubling of the hydrocarbon takes place also with toluene and cymene (*Rendiconti Acc. Lincei*, 1910, i., 645, meeting of May 22, 1910).

Though therefore in this paper Ciamician and Silber, making a kind of process to the intention, write:—"It seems to us not to be justified the assumption that more or less clearly shines through the recent publications of Prof. Paterno; that is, that the chemical reactions described by him are essentially different from ours," still it remains out of every discussion that Ciamician and Silber have only added some other examples to the reaction by us for the first time observed.

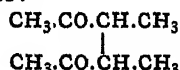
The fact of the re-doubling of the carbon chains, which yield their hydrogen in the reduction of ketones to pinakones, does not only take place with toluene, ethylbenzene, *p*-xylene, and cymene, but it manifests itself also with substances of different chemical structure. Thus from phenylpropionic acid we have obtained a dibasic acid, the diphenyladipic or dibenzylsuccinic acid:—



And from benzylcyanide we have obtained the nitrile of diphenylsuccinic acid (*Gazz. Chim. Ital.*, xl., [2], 324):—

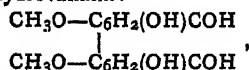


The transformation observed by Ciamician and Silber (*Ibid.*, xlv., [1], 255), by which, from methylethylketone, is formed a diketone:—



though the result may have been judged unexpected and really noteworthy, enters evidently into the reaction that we have observed.

In this argument we must note that in no case have we verified the addition of two aromatic nuclei, whence a special interest acquires to our eyes the transformation of vanillin into dehydrovanillin:—



this was observed by Ciamician and Silber (*Rendiconti Acc. Linc.*, 1912, i., 547); if confirmed, the same will apply to the production of diquinaldine from quinaldine and acetophenone, which we have recently announced (*Ibid.*, 1901, i., 101).

It is not improbable that the hydrogen of the benzenic group, which is not reduced by ketones, even in the case of mono-substituted compounds like phenol and benzoic acid, may become more interchangeable in a further substituted derivative, like vanillin and quinaldine.

(To be continued)

Tormentol.—A. Goris and Ch. Vischniac.—From the root of *Tormentilla* the authors have extracted a white silky crystalline product which they have called tormentol. Its composition is very complex, and not easy to determine. The formula of the anhydrous substance appears to be  $C_{33}H_{50}O_{10}$ . It is a saturated, neutral, non-nitrogenous product which does not combine with semi-carbazide nor with phenyl hydrazine, but gives ethers with acetic anhydride, &c. It melts at  $227^\circ$  to  $228^\circ$ . It turns the plane of polarisation to the right. On saponification with alcoholic potash it gives an acid and an alcohol, the melting-points of which are both higher than that of the original product; tormentol is thus both an ether and an alcohol.—*Bull. Soc. Chim. de France*, xvii.-xviii., No. 3.

# THE USE OF RADIO-ACTIVE SUBSTANCES AS FERTILISERS.\*

By WILLIAM H. ROSS,  
Scientist in Soil Laboratory Investigations.

## Introduction.

A FERTILISER may be conveniently defined as any commercial material which, when added to a soil that has been brought into suitable condition for the growth of plants, produces an increased yield in crop production. In producing this result a fertiliser may act in various ways, bringing about an improvement in the chemical, physical, or biological condition of the soil, and generally in all of these. An improvement in all these three classes of soil conditions may also be brought about by other farm operations, as by tillage, green manuring, and the rotation of crops. To what extent these latter operations should be supplemented, or even in a measure replaced, by the use of fertilisers, so as to lead to the most profitable returns, is a matter which has given rise to a great deal of controversy, and there still remain considerable differences of opinion on the subject. This is due in a large measure to the fact that the results obtained from experiments carried on locally and under special conditions of farming are often quoted as applying to the whole country and to conditions of farming of an entirely different type. It is quite evident, however, that any set rules governing the use of fertilisers in farm practice are only applicable when all conditions of soil fertility, climate, cultivation, and crop production are about the same. Fertilisers must therefore be used differently under different conditions, and it is universally admitted that when intelligently applied, where the conditions warrant it the use of the proper fertiliser brings profitable returns.

A great many forms of fertilisers are used, but all those commercial products which are recognised as of value in the fertiliser trade have the common feature of containing one or more of the elements—nitrogen, potassium, phosphorus, and calcium. These elements are therefore spoken of as fertilising elements.

It is further recognised that in a very general way the value of a material is proportional to the percentage of the fertilising constituent or constituents present in soluble form. Because of its wide distribution calcium can usually be obtained locally, and consequently it does not enter into the fertiliser trade in the same sense as the other fertilising elements. To each of the three remaining elements is given by common consent and as a trade practice a definite value per unit, which varies with the form in which the element occurs; the price set on a standard fertiliser, while thus in a sense an arbitrary one, is nevertheless determined in a scientific way by multiplying the percentages of the constituents present by their prices per unit and adding the products.

If nitrogen, potash, and phosphoric acid are absent, the fertilising value of the material as calculated in this way will be zero, and no material, with the exception of certain calcium compounds, as lime and gypsum, that does not contain one or more of the constituents referred to is recognised at present by agricultural scientists as having commercial value as a fertilising agent for general farming.

Notwithstanding these facts there have frequently been placed on the market from time to time various so-called fertilisers, which contain little or none of the recognised fertilising elements even in an insoluble form. As a rule these materials consist simply of ground rock, usually of volcanic origin, from various sources, and for which an arbitrary price is asked out of all proportion to the value of the small amount of the fertilising elements which may be present. Some of these materials, although exploited to quite an extent in the past, have later fallen into disfavour, and are now no longer used by anyone, but others of more

recent development are still being placed on the market under different trade names. One of these new materials, which is known as "radio-active manure," consists of low-grade uranium-radium ores, or ores from which the uranium has been extracted, and it is claimed to bring about, by virtue of its radio-activity, phenomenal increase in crop yields when mixed with barnyard manure and applied to the soil. Within the past few years the use of this material as a fertiliser has been quite extensively advertised in various parts of the world, and accounts have been given in various scientific publications of numerous results which have been obtained in pot and field tests using radio-active material from different sources.

The object of this Bulletin is to give a review of these results, and likewise an explanation of the property of radio-activity, in order that a conclusion may be reached as to the value of applying radio-active material to the soil.

## Properties of the Radio-Elements.

The properties of the radio-elements have been investigated by many of the leading scientists of the present day, and have consequently been determined with a degree of exactness and completeness which perhaps has never before been equalled in any other branch of science in the same length of time.

The following points with regard to these properties may be enumerated as having bearing on the fertilising value of radio-active material:—

1. An element is said to be radio-active when it has the property of disintegrating or changing into another element. This property of radio-activity as exhibited by radium, which is the best known popularly of the radio-elements, is one which is inherent in the atom. No substance can be radio-active which does not contain an element which would be radio-active if separated from the substance, and conversely, if a substance contains such an element it must be radio-active. Some of the radio-elements, like the ordinary elements, do not give off any rays, others give off one kind of rays only, while still others give off two different rays, each of which may differ from the single radiation, thus making altogether three different kinds of rays. No inactive substance can be made radio-active by exposure to any of these rays. The activity of a given quantity of a radio-active element, like uranium or radium, remains unchanged in whatever chemical or physical state it may exist, whether combined in a soluble or insoluble compound, and whether or not it may be mixed with any substance or substances whatsoever. It therefore follows that its activity can not be intensified by mixing with barnyard manure, as is sometimes claimed.

2. Radium is a product of uranium, and can not occur in nature in quantity exceeding the amount with which it is in equilibrium with uranium. For this reason the highest concentration of radium which can ever be found in any ore will amount to only one part of radium in 3,460,000 parts of ore. This quantity of radium is so small that if chemical tests alone had been applied neither radium nor any of its products could ever have been identified. There are physical tests, however, which are much more delicate than any chemical tests. Thus, when the spectroscopic test is applied to lithium, an element which according to chemical tests is of very limited distribution, it is found to be almost universally distributed, and in no spring water, for example, does the test fail to reveal its presence. The electroscopic test for radium is even much more delicate than the spectroscopic test just cited, and it thus happens that radium, which occurs in soils, for example, in such minute quantities, can nevertheless be identified in all soils. If the same delicate test could be applied to all the ordinary elements it is universally admitted that they too would be found in all soils and in much larger amounts than radium, for the reason that they occur in nature in much larger quantities. (The presence of the rare earths and other rare elements in all

\* Bulletin 149, U.S. Department of Agriculture, Bureau of Soils.

soils examined has been demonstrated by W. O. Robinson, of the Bureau of Soils; *Bul.* 122, U.S. Dept. Agr.). The ordinary elements could not have been discovered if this were not the case. Most soils differ but little in their radium content, as must follow from the fact that almost all rocks which do not contain uranium ores contain pretty much the same quantity of radium (Strutt, *Proceedings Royal Soc.* [A], 1906, lxxvii., 472).

On an average the radium present in an acre-foot of soil amounts to about 3.6 mgrms. (Moore, *Yourn. Ind. Eng. Chem.*, 1914, vi., 373). The radium present in one ton of carnotite ore containing 2 per cent of uranium oxide ( $U_3O_8$ ) amounts to 5 mgrms. To duplicate the amount of radium in an acre-foot of soil would therefore require about three-fourths of a ton of 2 per cent carnotite ore from which radium has not been extracted, and which brings about 80 dol. a ton wholesale. It is thus quite evident that to increase the radium content of the soil to any great extent by the use of carnotite or any other radium ore is out of the question as an economic proposition.

The chemical properties exhibited by an element in combination depends on whether the element occurs in a soluble or insoluble form. Thus the addition of a comparatively small amount of a soluble potash salt has a marked effect on the growth of plants, while the corresponding amount of an insoluble potash silicate would have little or no effect so long as it remained insoluble. As already explained, the property of radio-activity does not change in this way with the form of combination, and a given weight of radium in the soil has exactly the same activity as the same weight of radium in any other form of combination that can be added. The argument, therefore, can not be advanced that the radium in radio-active manure is in a more active form than that already present in the soil.

3. When a preparation of radium which has been freed from its products is allowed to stand for a time, the products are again formed, and finally reach a state of equilibrium with the radium. When this is the case the material has its greatest activity, and any preparation which is allowed to stand for a time always consists of a mixture of radium and its products. The first of the products to be formed from radium is a gas called radium emanation. Since radium itself gives off rays, while radium emanation is a product of radium, the activity of radium emanation in equilibrium with its products must always be less than that of radium in equilibrium with its products. It therefore follows that no preparation of radium emanation can be obtained which is more active than the radium available.

When the radium emanation is removed from a preparation of radium, the total radiation evolved from the two sources remains the same as that given off from the preparation before the separation. The total radiation has thus not been either increased or decreased by the treatment, and as far as the use of the rays is concerned it must necessarily be just as expensive, although possibly at times more convenient, to treat plants with radium emanation as with the radiation from the equilibrium amount of radium.

#### The Influence of Radio-active Rays on Plants.

Every physical agent known when exceeding a certain minimum intensity is able to affect in a marked degree the germination of seeds and the growth of plants. It would, therefore, be expected that the rays from radio-active substances when present in sufficient intensity would likewise have an influence on plant growth. A great many experiments have been made along this line, and the literature on the subject is already very extensive. Unfortunately, in many of the experiments which have been made no mention is made of the amount of radio-active material used nor of the intensity of the radiations emitted by it, consequently such experiments can not be duplicated by others, and the results reported are therefore of little value, for it could have been predicted that

a very intense radiation would have an injurious effect on plant growth, while radiations of moderate intensity might exert a beneficial effect. Furthermore, owing to an insufficient knowledge of the properties of radio-active rays, many experiments have been carried out in such a way that the effects which were attributed to the rays could not possibly have been due to this influence.

The most extensive experiments in this field which have been described in this country were carried out by Gager at the New York Botanical Garden ("Effects of the Rays of Radium on Plants," *Memoirs of the N.Y. Botanical Garden*, 1908, iv.). In one set of pot experiments a quantity of polonium (activity not given), enclosed in a sealed glass tube, was inserted in the soil at the centre of the pot, with the end containing the radio-active material about 10 mm. below the surface. Twelve grains of wheat were then planted without soaking in the soil around the tube. Three other pots were also prepared in the same way with the same number of wheat grains. In one of the pots was placed a tube containing 10 mgrms. of radium bromide of 1,800,000 activity; in another, a tube containing 10 mgrms. of radium bromide of 1,500,000 activity, while the remaining pot was used as a control. On the fourth day measurements were made of the height of the seedlings, and it was found that the average growth was greatest in the pot containing the polonium and least in the control pot. It is known, however, that polonium gives off alpha rays only, and that these rays are so lacking in penetrating power that they could not have penetrated the walls of the glass tube in which the polonium was contained, much less could they have penetrated the intervening soil which separated the tube from the planted seeds. (In this connection the author himself states:—"I am unable to explain how physiological effects can be obtained with radio-tellurium [polonium] in a sealed glass tube, for this substance gives off only  $\alpha$  rays, and these are not thought to be able to pass through the glass walls of the tube. The results, however, were constant and decided, leaving not the slightest doubt as to the physiological efficacy of the preparation." *Loc. cit.*, p. 144). If the experiments were carried out as described the seeds in the pot containing the polonium tube must have been as free from any radio-active influence as those in the control pot, and the marked increase noted in the growth of the seedlings in this pot could not have been due to the presence of the polonium tube, as claimed by the author, but must be attributed to some other influence.

From the way in which other experiments were carried out it seems reasonable to suppose that other results were likewise incorrectly attributed to radio-active influence. Thus it was concluded "that freshly fallen rain water tends to retard the growth of roots of beans (*Lupinus albus*), and that the effect is due to the radio-activity of the water" (*loc. cit.*, p. 178). It was further observed from other experiments that "the growth in length of radicles of *Lupinus albus* is uniformly accelerated in an atmosphere containing radium emanation" (*loc. cit.*, p. 156). The intensity of the radiation was not given in either case, but it was indicated, and it is undoubtedly a fact that the intensity of the radiation in the latter experiment was much greater than in the former. It would thus seem that, as measured by the growth that takes place without any radio-active influence, a weak radiation retards, while a stronger radiation stimulates the growth of certain seedlings. This is contrary to experience and to the general conclusion reached by the author that "the rays of radium act as a stimulus to protoplasm. Retardation of growth following an exposure to the rays is an expression of over-stimulation. Acceleration of growth indicates stimulation between a minimum and an optimum point."

Experiments were also described in which seeds and seedlings were exposed in a six-inch pot to the radiation from 10 mgrms. of radium bromide of activity 1,800,000. A preparation of 0.5 gm. of radium bromide of activity

10,000 was also used. Both retarding and stimulating effects were observed, depending on the seedlings used and the conditions of the experiments. It would be expected that with a radiation of the intensity given by these preparations a marked effect would result, as was observed. The experiments are thus of scientific interest, but they do not give any indication that radium can be of any practical value in general farming. To duplicate the experiments on a large scale would require a quantity of radium which is not available.

Many experiments on the influence of radio-active matter on plant growth have also been made by Stoklasa (*Comptes Rendus*, 1912, clv., 1096; 1913, clvi., 153; 1913, clvii., 879, 1082). In one set of experiments there was observed the effect of adding varying amounts of uranium in the form of uranium nitrate to a given quantity of soil. Using plants of clover (*Medicago albus*) a maximum increase in growth of 24 per cent was obtained when 1 part of uranium was used to 1,310,000 parts of soil. But the presence of lead in the form of lead nitrate was found to be even more stimulating in its action, since a corresponding increase in growth was obtained with a concentration only one-eighth as great as the quantity of uranium which gave best results. Lead, however, is a rayless element, and the effects observed with it must have therefore been due to its chemical properties. As a soluble salt of uranium had to be used to give the effects observed, it is reasonable to conclude that these effects are likewise due, in a large measure at least, to the chemical properties of the uranium rather than to its radio active properties. Further evidence of the truth of this statement will be given later.

In other experiments Stoklasa (*loc. cit.*) made a study of the change in rate of nitrogen fixation brought about by bacteria (*Asiobacter chroococcum*) when cultures of these bacteria were placed in an atmosphere containing radium emanation. In carrying out the experiments two litres of air, having an activity of 150 Mache units, were passed daily into the vessel containing the cultures, and there resulted from this treatment a marked increase in the amount of nitrogen fixed by the bacteria. (The unit now generally used for expressing a quantity of radium emanation is called the *curie* or the *microcurie*, and is the amount of emanation in equilibrium with 1 grm. or 1 microgram. of radium. One microcurie per litre equals a concentration of about 2700 Mache units). It was further observed that the time of germination of seeds was shortened and an increase in the development of plants resulted when watered with water having an activity of from 30 to 2000 Mache units.

Using a concentration of emanation about thirty times as great as that given by Stoklasa, Fabre likewise observed favourable results in the germination and growth of seedlings (*Comptes Rendus Soc. Biol.*, 1911, lxx., 187). Many experiments on the influence of radio-active matter on plants have also been made by other investigators, but, unlike the results just cited, the effects reported in the majority of cases were deleterious rather than beneficial.

As radium emanation is an inert gas, the results obtained with its use can not be due to its chemical properties, as in the case of uranium, but must be attributed to its property of being radio-active. It is thus necessary to conclude that radio-active material does have an effect on plant growth, and that when a certain concentration, but not too great a concentration, is used stimulating effects are to be expected, in some cases at least; in fact it is to be expected, although not yet clearly demonstrated, that in greenhouse practice and in botanical research, where the results obtained might justify the expense involved, the radio-elements may prove of very great value, as they have done in other branches of science. When consideration, however, is taken of the scarcity of these elements, it does not follow from any experiment so far described that such elements can have any practical application as a fertiliser in general farming. To increase the activity of the atmosphere above the soil with radium emanation

would not be feasible in field practice, neither would it be practical to add such a quantity of radio-active material to the soil that the emanation in the underground air would be increased to even the very low concentration used in Stoklasa's experiments, and the same may be said with regard to making irrigating water radio-active.

(To be continued).

## CHEMICAL RESEARCH. GOVERNMENT AID PROMISED.

A JOINT deputation from the Royal Society and the Chemical Society was received by the President of the Board of Trade and the President of the Board of Education at the Board of Trade Offices, 7, Whitehall Gardens on Thursday, May 6, 1915. With Mr. Runciman and Mr. Pease were Dr. Addison, M.P., Sir H. Llewellyn Smith, Sir L. A. Selby-Bigge, Mr. Ogilvie, Dr. Heath, and Mr. Percy Ashley.

The deputation, which was introduced by Sir William Crookes, consisted of Professor A. W. Crossley, Dr. H. J. H. Fenton, Dr. M. O. Forster, Professor W. H. Perkin, Professor W. J. Pope, Professor Arthur Schuster, Professor A. Smithells, Professor J. F. Thorpe, and Mr. R. W. F. Harrison, representing the Royal Society; Dr. Alexander Scott, Professor F. G. Donnan, Professor Percy W. Frankland, Professor J. C. Philip, Sir William A. Tilden, and Dr. Samuel Smiles, representing the Chemical Society; Dr. A. Chapman (President of the Society of Public Analysts), Dr. G. G. Henderson (President of the Society of Chemical Industry), Professor Jackson, and Mr. Edward W. Voelcker, representing the Institute of Chemistry.

Professor W. H. Perkin, Sir William Tilden, Professor Percy Frankland, Professor W. J. Pope, and Dr. Martin O. Forster spoke in support of memorials from the Royal Society and the Chemical Society which had been submitted to his Majesty's Government on the position of the chemical industries, and the steps which might be taken to improve their status and efficiency in the United Kingdom. The speakers drew attention to the fact that the comparatively backward state of certain industries in this country is due to a failure to realise that modern industry to be successful must be based on scientific research, and to the lack of association between manufacturers and science, combined with a want of scientific knowledge and appreciation of the importance of scientific work amongst the public generally, and the lack of organisation among the various chemical and allied industries.

The deputation advocated Government assistance for scientific research for industrial purposes, the establishment of closer relations between the manufacturers and scientific workers and teachers, and the establishment of a National Chemical Advisory Committee for these purposes.

### Government Sympathy.

Mr. RUNCIMAN, in reply to the deputation, pointed out that the Board of Trade fully appreciated the extent to which national industrial progress is dependent upon the utilisation of the services of men of science, and the importance of provision for the thorough training of a very much larger number of industrial chemists than are at present available. He agreed with the views expressed as to the need of closer co-operation between manufacturers and scientific workers and teachers. The war had shown the weakness of our position in certain important respects, and he was in full sympathy with the general views expressed by the deputation. The actual proposals would receive careful and sympathetic consideration.

Mr. PEASE informed the deputation that the particular problems to which they had drawn attention had been

present to the Board of Education for some time past, and that a scheme had been approved in principle by which substantial additional assistance would be given by the Government to scientific education and to industrial research. He hoped that, though the funds immediately available might not be large, they would be sufficient to enable an organisation to be brought into being at an early date, which would be capable of expansion subsequently. Mr. Pease further expressed his appreciation of the offer of assistance and advice by members of the two societies represented at the deputation.

Sir WILLIAM CROOKES expressed the thanks of the deputation for the sympathetic reception which they had received.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, April 29, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

*"Transmission of Infra-red Rays by the Media of the Eye, the Transmission of Radiant Energy by Crookes' and other Glasses, and the Radiation from various Light Sources."* By H. HARTRIDGE and A. V. HILL.

The different eye structures were found by us to absorb infra-red rays of different length to approximately the same extent as would a layer of water of the right equivalent thickness. From the values of the percentage absorption of water at different wave-length we therefore calculated the amount of heat absorbed by cornea iris and lens. The heat absorbed by the lens was found to be too slight for cataractous changes to be due to direct action. The condition might still be caused, as Parsons suggested, by impairment in the nutrition of the lens, brought about by the action of heat rays on the ciliary body and iris. Samples of Crookes' glasses were tested by us, and were found to absorb the heat waves strongly, and also to some extent the ultra-violet.

*"Surface Tension and Ferment Action."* By E. BEARD and W. CRAMER.

The action of a ferment on a substrate is retarded or inhibited by extending the surface of the system in which the reaction proceeds. This effect has been studied in some detail in the system cane sugar—invertase.

*"Surface Tension as a Factor controlling Cell Metabolism"* By W. CRAMER.

The considerations developed in this paper are based on the fact, demonstrated experimentally, that the action of ferments is conditioned by surface tension. The great surface development in the cell and the living organism must therefore produce conditions which markedly affect the action of ferments *in vivo* when compared with their action *in vitro*.

It is shown how the cell may, through the factor of surface tension, control and regulate its metabolism. It is thus possible to form a conception of the chemical organisation of the cell without having to assume the existence of hypothetical membranes in the cytoplasm which are supposed to surround the different chemical systems and separate them from each other.

Lastly, it is pointed out that if the conceptions formulated in this paper are correct, substances which are strongly surface active, but which do not affect protoplasm chemically, should exercise a profound effect on the metabolism of the cell. This expectation is realised in the action of narcotic and cytolytic substances.

## INSTITUTION OF CHEMICAL TECHNOLOGISTS. (LONDON SECTION).

Colonel CHARLES E. CASSAL, V.D., President of the Institution, in the Chair.

(Concluded from p. 227).

Dr. L. T. THORNE, Ph.D., F.I.C.—Mr. President, I cannot profess to be able to follow many of the speakers who have preceded me in the high flights of oratory to which they have treated us, but I can claim to have a tolerably long experience in chemical technology, and I have also to admit that I owe a considerable amount of debt to the country that has been very strongly dealt with to-night. At the time I studied chemistry, which was a long time ago, we had in English chemical colleges practically no training in research work. To my mind the research work of the chemist is of the greatest importance. I was compelled to go to Germany for my finishing teaching, and there I came under the hand of some of the leading German chemists of the time. I do not hesitate to express my great debt to those men. To me the commencement of this war and its conduct has caused the deepest pain, because I have had for a great part of my life most intimate friends, for whom I have the greatest respect, among the Germans. Although I agree with a great deal which has been said, although one cannot understand the degradation to which Germany and Germans have descended, I still cannot go quite as far as some of the speakers, especially my friend the President, have gone to-night.

Now let us turn from the ethical side for a moment, which I mentioned because it gives me the key to that on which I wish to speak. I returned from Germany in 1880, and I think I was about the first to call the attention of England to the need of waking up in regard to technical chemistry. I pointed out then that we had no technical colleges at all, whilst Germany had dozens of such colleges. Even then many of the German institutes were on a scale at least equal to that of the best of our present-day technological schools. Since then we have put up polytechnics and technical schools, but still even now we do not recognise the point of view that has been the secret of the schools of German technology. We do not recognise the real value of thorough research training, accompanied by technical training in the cognate branches of technology. It has been said that in our colleges the degree is the great thing. That was equally the case in the German colleges, but the great difference was that in the English colleges the degree has been obtainable mainly by theory, whilst in the German colleges from the earliest times the degree could only be obtained by showing capacity for and having carried out research.

From the point of view of the technologist, and I have been one for over thirty years, I do not hesitate to say that the particular point in my chemical training on which I place the highest importance is that of scientific research. The chemical technologist who is to take a true position in the works must have that groundwork of chemical research, because the main, or almost the main, purpose of the works technologist is to be able to carry out the researches that are always necessary in the development of the technical industries. In Germany we had everything pointing in that way. The second point that was of supreme importance was that the manufacturer, especially the dye manufacturers, had already recognised the value of that highly trained chemical technologist and research chemist. Even when I was in Germany some works had something like eighty or a hundred trained university men in their works. The board of directors or the heads of the firms were themselves highly trained men. When we come to this side of the question in England we find absolutely the reverse. Even at the present time, when the attempt is to be made to regain the dye industry for England, we have so scandalous a state of things that the prospectus of the new dye company contains no man on the board



who has a scientific knowledge of the subject he has to deal with. The chemist, on whom the whole matter is dependent, is relegated to a back room. Unless we wake up to the fact that where we have to deal with scientific manufacture we have to place the actual control of these scientific works in the hands of scientific men, we cannot fight against our competitors. It has been said that we can take the dye industry by force. That may sound nice, but it is not practical. You cannot take an industry like that. You cannot take the brains of the Germans away, or devote to our works their brain power, but you must take to a certain extent their method in developing the industry. The position of the works chemist is too often a scandalous one. The number of works where the chemist is given a free hand to spend money within reasonable limits as required, and is backed up by the head of the firm, is, lamentable to say, very small indeed, but it is necessary that it should be augmented. Mr. Dibdin has shown you how scandalous is the lack of appreciation of scientific work, and of the position that it ought to take, in the case of the London County Council. We must take the view that science must be recognised more, that the position of chemical technologists must be more pressed on the view of the commercial man, and unless we can effect that, any protection or anything else will not enable us to maintain our supremacy.

To give one instance in the dye industry. As long as that dye industry had at the head of the firm the man who initiated it in England and carried it on successfully, Dr. Perkin, a research chemist of the highest genius, so long was it maintained in England against the competition of Germany. As soon as it became a public company and the board consisted merely of commercial men, then England began to fall back and Germany came forward.

Unless we can recognise the state of things, and recognise the need for following in the footsteps of our enemies, we shall not maintain or regain our position, and our present efforts will be futile.

Mr. PERCY C. H. WEST, F.C.S. (Secretary)—Mr. President, the last speaker has referred to the value of technical research. We know that the organic chemical industry in Germany is of enormous size, and we know that this country occupies a negligible position. I think Dr. Thorne is right in pointing out that this industry is founded on research. As far as quantity is concerned we may produce a smaller amount of purely scientific research than the Germans, but the value of it is no less great. It has been said that our intellectual output in this direction so far as value is concerned is not inferior to that of other nations, but I do not intend to speak in support of that view. It is not much smaller, I think. Thus the capacity for research exists in us. A good impression of the amount of technical chemical research done in Germany can be obtained from the patent applications in this country. For example, in 1884 to 1888 in Class 2 (organic acids, salts, and other compounds) there were 240 applicants and roughly 400 patents. The average works out at 1.6 patents per applicant per four years, but the applications in the names of four German firms works out at 63. They are thus responsible for 16 per cent of the applications in this class. In 1889 to 1892 these four firms had 189 applications. In 1893 to 1896, 267, and in 1904 to 1908, 356, out of about 1900 applications. It might be argued that the law requires that a patent shall be taken out in the name of the inventor, and hence that in the case of British applicants the patents would be in the names of individual inventors, but the President pointed out that the agreements are such that in law probably the employer is held to be the inventor. The inventor's name appears in the application, and if these firms had been interested in these things, if they promoted the patents—if they were the prime cause of the patents being applied for—they would in any case have insisted on their name being in the application as co-applicants. The three largest British firms engaged in this industry were responsible, solely or as co-applicants, in the period 1904-1908, for 18, 5, and 3

applications. The classification has been altered. In the class called "2 iii. dyes, &c." in 1912, there were 426 applications. Of these, 39 presumably are in the names of British applicants, that is, there is some possibility that they were applied for by British subjects. Thus you have 426 applications, 39 being by British subjects. Four firms account for 155 of these. These four account for 38 per cent. That, I think, is a clear indication of the way the Germans look on research. It indicates the intellectual output of the industry. We know that the consumption of dyes in this country is believed to be three millions, of which two millions are imported from Germany. It is necessary if we are to have a chemical industry that we should encourage research, as the material output is intimately bound up with the intellectual output. It is curious that in this country but little value is placed on research. Research is a gamble. Individual research may lead to nothing. We are prepared to take our gambles—some do it on horses or the Stock Exchange, but every body agrees that chemical research is a gamble. In certain cases people finance research. They finance it,—but do they finance the right people? They go in for what are regarded as epoch-making inventions. Epoch-making inventions do not make fortunes, but it is the small inventions that do. Of the applications for patents by these German firms many are for small inventions, but they are of value. Many are stepping stones. Many are in the nature of blocking patents. The Patent Act of 1907 was designed to restrict these blocking patents, but it had no effect in this direction. If you take out a patent in a field that is covered by an individual firm, it is opposed. If the opposition has no possibility of success, the grant will be opposed just the same. The Germans in business are carrying out their operations with the same object that they have in view and by the same methods by which they are carrying on the war. They will crush you or buy you out. They are prepared to buy you out, but they will crush you if they can. That is the point. They recognise the value of research, whereas here it is regarded as unremunerative labour. I was speaking to a director of a concern engaged in the production of a material which had to be made up to a specification. He said "I always regard chemistry as a toy; I do not think there is much in it—it is unproductive labour." I said, "What about the ledger clerks?" He said, "Of course, they are doing something." I said, "Yes, they are, is their labour productive?" He said, "I could not get on without them." I said, "Could you run the works without chemists?" He said, "No, perhaps not, but we used to." I was acquainted with their material before they employed chemists, and if anyone needed chemists the so-called tests indicated that they did. Many other people regard science in the same manner as he.

My point has been to urge that there is a need for research and generally for a better recognition of the value of chemistry, and to this end we must educate the directors and financiers. Some of us know what they are: they have no recognition of the value of these things. There is one other matter on which Dr. Thorne supported me, or rather on which I support him. Mr. Darling said the cousins of proprietors are put into the works, and that is so. They are given a classical education and they want to make money. They have not that insight which the men who build up the business have, and they have not been given an education which causes them to realise the value of the chemist. Hence in their view and in their works the chemist occupies an unimportant position. Then Mr. Darling also referred to the meanness of the chemical manufacturers in the matter of pay. There is no need to refer to that for it is generally known. Mr. Dibdin has referred to the London County Council. It might be thought that the London County Council would be on a somewhat higher plane than a board of directors, but we see them acting as a bad board of directors in dispensing with their chemical staff or putting it under the nominal control of persons who are totally unacquainted with

chemistry because their training has been such that they are unable to appreciate the value of science. There can be no better illustration of the public attitude towards the chemical technologist than the case to which Mr. Dibdin has referred.

Dr. FRANK L. TEED, D.Sc. (Lond.), F.I.C. (Vice-President), Public Analyst for the City of London, &c.—Mr. President, the subject for discussion is the Future of British Chemical Industry, and I fancy one or two of the speakers have wandered away from it, possibly on account of the largeness of the subject and the difficulty of prophesying. There may be no future for it, or a brilliant future. We have been discussing the future of the industrial chemist rather than that of chemical industry. A meeting cannot pass cut-and-dried resolutions that English manufacturers or chemists should do this or that. We have such a huge mass of material to consider. We have to consider the education of the chemist and we have to consider whether any protection of any kind will make the chemical industry flourish. There you come into the maze of politics. You cannot expect the meeting to come to a unanimous conclusion. I ask this meeting to suggest to the Council of this Institution that they should appoint a committee to sit from time to time to consider the many questions involved and, when it is thought desirable, to report the conclusions they have arrived at. Each speaker has opened a wide field—the question of education and remuneration, and the possibility of the dye question, which is one of the smallest chemical industries. We wear three or four suits of clothes in a year, but we consume drugs to the value of the dye in our clothes to a much greater extent. We use metal to a greater value than that of the dyes which we consume. The dye question seems to me a minor point. There are three million pounds worth of dyes used in the kingdom, and there are forty-four millions of people; that means a very small expenditure per head—that is about one-fifteenth of a pound, *rs.* 4d. per head. If you consider the food question, most of us on spirits alone expend more than *rs.* 4d. in the course of a week. I suggest that we ask our Council to take it into consideration, and to appoint a committee to look at the various aspects, not merely to go into a branch like the aniline dyes, but to take all the trades generally. The extraction of ores is treated by a particular class of chemists termed metallurgists, not usually classed as industrial chemists. I throw this suggestion out to keep a permanent eye on the future.

The PRESIDENT—I will accept Dr. Teed's suggestion for a permanent committee to be appointed to watch the possible developments in the directions indicated. I accept the suggestion on the part of the Council.

Dr. L. T. THORNE, Ph.D., F.I.C.—Might I say one word with reference to the matters referred to by Mr. West. In the four companies which he referred to the chemists employed number over 800, and the directors number amongst them a large number of *scientific chemists*. I believe these boards recognise that if one chemist out of, say, twenty makes a discovery leading to a successful patent they are repaid. They do not expect every chemist to turn out researches by the dozen, as most of our English firms seem to do.

The PRESIDENT—I do not propose myself to add anything further to the discussion, but I should be glad to know if anyone else desires to address the meeting.

Dr. WALPOLE, D.Sc. (Mel.), F.I.C.—I did not dream I should speak when I came in, but there are one or two points raised in this discussion to which I should like to refer. When I started trying to earn a living as a chemist I got a university degree, and I had enough money to live for six months, and I thought I would go to Germany. I answered every advertisement, and offered to go for nothing. I could not get any work although I offered to work for nothing. I got no opportunity whatever. I do not think I need labour the moral. Mr. Dibdin has told us a lamentable story of the cement industry. I say that it is only by the education of the chemist, supplemented

by the education of the employer, that it will be possible successfully to fight Germany.

Mr. J. J. EASTICK, A.R.S.M., F.I.C.—Mr. President, I have nothing special to say. I am in an off-shoot of chemistry; the industry with which I have been identified is sugar. This meeting, I take it, desires to do something practical. I was pleased to hear that you accepted the suggestion on behalf of the Council to have a permanent committee. I hope they will arrive at some conclusion which will benefit the industries of England. I understand from what we have heard to-night that one thing we ought to do is to pass a vote of censure on ourselves as chemists for our lack of enterprise and of energy. I blame ourselves to a large extent. I do not go so far as to blame the manufacturers and directors. Take the position we are in to-day. The two things that frightened our Government were sugar and aniline dyes. They saw the country was going to have a famine, or something approaching it. To listen to these speakers one would think we could not make one or the other. But take ourselves back sixty years. Who held the premier position? England, both in aniline dyes and sugar. In dyes, they originated here, not there. Why did we lose our premier position? I think the whole thing hinges on that; if we solve that question we solve the question whether we are to regain that position in the future. I mean it is not a question of politics, for I blame both parties. I say it because we have always had a conspiracy by the German States, by the patrons of industry in Germany and the whole German State, to crush every industry we have. They have tried to annihilate the sugar industry and the dye industry. It is our fault; if we had taken steps to counteract the measures they took things would have been different. We knew they were giving bounties and subsidies; we knew they were levying such high taxes to fight England. They considered what extra profit their manufacturers could make on sugar; it amounted to five millions, and it was devoted to crush English sugar. The same thing took place in the dye industry. The dye industry is a small stream. We put it down at three millions, but it is less than that. It is an important thing that we held the premier position, but allowed ourselves to be ousted. It is because we allowed this gigantic trust or conspiracy to arise in Germany and gradually crush the English manufacturer. The English manufacturer had no chance. The English manufacturer has not had money to go into research; his money has been extracted from his pockets and put into the pockets of Germany. (Hear, hear.) I do not blame the manufacturers in this country. I say in some cases chemists have gone into the works and, as Mr. Darling pointed out, they have not been fit—their training has not enabled them to take a proper position in the works. I do not mind saying that when I left college I went into a sugar works and there was an instrument on the table. It was for polarising sugar solutions. I did not recognise it—I did not know what it was for. It was three days before I found out that they used an instrument for polarising sugar solutions, and I was five years at college. Mr. Darling belongs to a technical college, and I was pleased with what I heard of the college from which he comes, and I sent my two sons there. My experience is, when I have taken an assistant who is a university man, that he has not got that training which enables him to take an immediate position in the works; he must go through a period of probation. The colleges should make themselves practical. There should be a period of probation in some works, otherwise the university man goes into a works and he is asked to do this or that, and he makes a failure: he does not recognise the polariscope, therefore he gets into bad odour. He does not understand his business.

The PRESIDENT—I am going to ask you, gentlemen, to pass a special vote of thanks to the Institution of Mechanical Engineers for their hospitality in allowing us to use their hall for this meeting. (The vote of thanks was unanimously passed.) I thank you for your attend-

ance, gentlemen. We have had an interesting and satisfactory discussion, which I hope will be published.

Mr. WILLIAM THOMSON—We should pass a vote of thanks to the President, who has placed before us the subject of debate in so excellent a manner. I think the result of that debate has been exceedingly interesting. (The vote of thanks was unanimously carried).

The PRESIDENT—I thank you for your courtesy, gentlemen.

# PHYSICAL SOCIETY.

Ordinary Meeting, April 23, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER, "On the Theories of Voight and Everett regarding the Origin of Combination Tones," by Prof. W. B. MORTON and Miss MARY DARRAUGH, was read by the former.

Voight connects the existence of difference and summation tones with the fact that the stationary points of the compound vibration-curve, when the primary tones have equal energies, can be grouped in a certain way on sine curves, which recur in the periods of these combination tones. As against this view it is urged—(1) That, the same points can equally well be grouped on a whole series of curves with other frequencies; (2) that the distinctness of the combination-tones would on this theory vary greatly with phase-relationship of the primaries; (3) that the tones would disappear when the energies of the primaries are not very unequal. Voight applies a similar method to the case where the upper tone is weak compared to the lower to account for Koenig's second beat-tone. The first of the above objections again applies.

Everett supposed that the distortion of the vibration-curve in passing through the ear would bring in the note whose frequency is the highest common factor of the primary frequencies. The effect of a special kind of distortion has been tested, consisting in a proportional reduction of ordinates in one direction. The result does not confirm Everett's contention, but shows the appearance of the summation and difference tones.

## DISCUSSION.

Mr. F. J. W. WHIPPLE thought the matter was an extremely interesting one, and that the type of distortion assumed by the authors was very feasible. He suggested that an amplification of the theory might be applicable to musical instruments. For example, much of the beauty of the tones of a violin was attributed to the presence of many additional notes besides the fundamental. Quite possibly an asymmetry in the vibrations of the sounding board was responsible for the addition of combination tones of the higher harmonics.

Mr. D. OWEN referred to the case of a man who had no ear-drums, but could nevertheless hear combination tones, which Prof. Morton had cited as an instance in which unsymmetrical vibration of the receiving system could not be the cause of these tones. He presumed that this subject was very deaf, and that any sounds which he could hear at all would be very loud. Consequently, there would be violent displacements of the bones of the ear, and one would expect considerable asymmetry in their vibrations.

Dr. RUSSELL thought that the authors had without doubt completely demolished Voight's theory, which seemed to have no physical basis whatever. With regard to the unsymmetrical vibrations of the drum, he supposed Helmholtz in his investigation had treated the tympanum as a thin plate, but the attached bones and adjacent fluid would render the problem much more complex.

Prof. S. P. THOMPSON communicated:—Though it is well to discuss the theory of combination tones it is much more important to be certain first *what are the facts*, to account for which some theory is required. Hence I raise

the vital question of what the facts are: According to von Helmholtz, the combination tones are of two kinds, differential and summational. That is to say, when two tones of respective frequencies  $m$  and  $n$  are simultaneously sounded, the ear hears the *difference* tone, of frequency  $m-n$ , and the *summation* tone, of frequency  $m+n$ ; and these are ear-manufactured, and cannot be heard in any resonator, and have nothing to do with beats. According to Koenig, the combination tones are simply beat-tones (and were so regarded also by Thomas Young), and cannot be heard in any resonator. If any supposed combination tone is heard in a resonator, that is a proof that it exists objectively in one or other of the two primary tones, and that, therefore, one or both of the two primary tones is not a *pure* tone, but contains the alleged combination tone as a harmonic. Koenig found that beats and beat-tones fall into two series (called superior and inferior), corresponding respectively to the two remainders—positive and negative—to be found by dividing the frequency of the higher tone by that of the lower tone. Thus, let the two primary frequencies be 40 and 74. Then, if we divide 74 by 40, it goes once with a positive remainder of 34, or it goes twice with a negative remainder of 6. Koenig heard, in these circumstances, a rapid beat (inferior) of 34 and a slow beat (superior) of 6. If we take as primaries the note of frequency 3328 and the note 2048, there will be heard, according to von Helmholtz, the difference tone 1280 and the summation tone 5376. According to Koenig, there will be heard the (inferior) positive remainder 1280 and the (superior) negative remainder 768. As a matter of fact, two tones are heard, the stronger being 768 and the weaker 1280. The summation tone 5376 is not heard at all. If we take, again, two forks giving 2304 and 1024, the only combination-tone heard is 256, which is neither difference nor sum. It is the (positive) remainder heard by dividing 2304 by 1024. Voight's theory accounts for this, von Helmholtz's does not. Koenig, who in his lifetime tuned with his own hands some tens of thousands of forks, and used the beat-tones to determine the tuning of his high-frequency forks of inaudible pitch, had never been able to hear any tones corresponding to the summational numbers. They simply do not exist if the primary tones are pure.

Prof. MORTON, in reply, said he could not say how far combination tones might be produced by the sounding board of a violin. They certainly could be produced by the membrane of a telephone receiver. He had not quoted the man with no ear drums as a case in which asymmetry was not responsible for these tones, but only as one in which we had to go further back than the tympanum for the seat of this asymmetry. A German author had tried to locate this in the motion of the fluids of the ear. Helmholtz's investigation of the vibration of the drum was even less satisfactory than the Chairman had supposed, as he treated it simply as an oscillating particle. The analysis had more recently been extended to the case of a membrane and similar results obtained, but even this was still remote from the actual case of the ear drum.

A paper, entitled "*Experiments on Condensation Nuclei Produced in Gases by Ultra-Violet Light*," was read by Miss MAUD SALTmarsh.

1. Nuclei produced in air by ultra-violet light which has traversed a few centimetres of air are not affected by an electric field of 50 volts per centimetre.
2. The nuclei are equally effective in producing condensation of water, toluol, and turpentine vapours, and they are formed even by light which has traversed 50 cm. of air.
3. Alcohol vapour condenses without expansion on much smaller nuclei than does water vapour.
4. No nuclei were formed by the light unless oxygen or  $\text{CO}_2$  was present in the gas.
5. No trace of  $\text{H}_2\text{O}_2$  could be detected in the clouds formed on the nuclei.

6. Oxygen containing ozone also contains nuclei for condensation, and these nuclei have similar properties to those formed by ultra-violet light.

7. The nuclei can be destroyed by heating the air containing them.

It seems probable that the nuclei formed by ultra-violet light do not cause condensation by virtue of any particular chemical composition, but that they are particles large enough to act like dust particles as centres round which condensation can begin.

#### DISCUSSION.

Prof. O. W. RICHARDSON said the author had succeeded in eliminating a number of substances to which these effects had from time to time been attributed. The method employed was extremely sensitive, one or two ions being easily detected. Of the various substances eliminated the only one which he was not quite certain of was ozone. The elimination of this seemed to rest on the results of Lenard and Ramsauer. Did the author think these results were absolutely conclusive?

Mr. D. OWEN said that the explanation of the action of ozone in causing cloud formation was difficult if regarded as a direct effect. Possibly ozone acting on water vapour might give rise to hydrogen peroxide, in which case the suggestion of Mr. C. T. R. Wilson of a lowering of the saturation vapour pressure would apply. However, the failure, in the case of fogs produced by ultra-violet light, to detect hydrogen peroxide by the titanium oxide test, which, according to Dr. Senter, can detect one part of hydrogen peroxide in ten millions, seemed to exclude the action of hydrogen peroxide. As a possible alternative, the agency of oxides of nitrogen might be suggested. It would be of interest to test whether the phenomenon occurs when nitrogen is entirely excluded. In conjunction with chemical tests of amount present, quantitative data enabling the resulting lowering of the vapour pressure to be calculated should enable the problem in question to be definitely solved.

Dr. H. BURNS remarked that the detection or identification of hydrogen peroxide was not always easy. In experiments of the kind described in the paper effects might be ascribed to hydrogen peroxide which were really due to nitrogen oxides. Such oxides would be produced when air was drawn through hot quartz tubes, and might help to account for the peculiar observations mentioned in the last part of the paper.

Miss SALTMARSH, in reply, was not aware of any work having been done on the effect of oxides of nitrogen in producing condensation nuclei. In reply to Prof. Richardson, Lenard and Ramsauer had not stated that ozone was ineffective. They laid great stress on the presence of minute quantities of impurities. They attempted to get rid of these by condensing them out at low temperatures. They held that the ozone reacting on these traces of impurities was instrumental in producing the effects.

A paper, entitled "*On the Self-induction of Solenoids of Appreciable Winding Depth*," by Mr. S. BUTTERWORTH, was taken as read on account of the lateness of the hour.

The existing formulæ for coils of this type—viz., those of Rosa and Cohen—are shown to be inaccurate, the error amounting to one fifth of 1 per cent for the best formula when the winding depth is one-tenth the diameter of the coil. For greater winding depths the error is larger. The inaccuracy in Rosa's formula is due to the neglect of curvature in correcting for thickness, while in Cohen's formula the error is due to the approximate method of development.

New formulæ are developed by methods which are free from such approximations, and which apply to any coil for which the length is greater than twice the diameter, and the winding depth is less than one-tenth the diameter. These formulæ are capable of giving eight-figure accuracy.

Simplified formulæ are also given which are suitable when only four-figure accuracy is required.

## NOTICES OF BOOKS.

*Directory of Paper Makers*, 1915. London: Marchant Singer and Co.

THE Paper Makers' Directory for 1915 contains carefully compiled and authenticated lists of paper makers in the United Kingdom, and also of trade designations, including both actual water-marks and trade names. A short section on paper trade customs has been added, and a complete directory of paper makers suppliers.

## MISCELLANEOUS.

Imperial College of Science and Technology, 1915.—The London County Council will be prepared to award for the Session 1915-16 a limited number of free places at the Imperial College of Science and Technology, South Kensington, S.W. The free places will be awarded on consideration of the past records of the candidates, the recommendations of their teachers, the course of study which they intend to follow, and generally upon their fitness for advanced study in science as applied to industry. Candidates will not be required to undergo a written examination. It is possible that the free places may be extended to two or more years. The conditions are as follows:—(a). Parents (or guardians) of candidates must be resident within the administrative County of London, except in the case of self-supporting candidates over twenty-one years of age on July 31, 1915, who must themselves be resident within the county. (b). Candidates must be day students at an approved institution, and must have been in regular attendance at an appropriate course of study for the last two sessions. (c). Candidates will be required to show that they are qualified to enter on the fourth year of the course of study selected. The fourth year of a course at the Imperial College is in the nature of a post graduate course. Application forms (T. 2/268) may be obtained from the Education Officer, L.C.C. Education Offices, Victoria Embankment, W.C., and must be returned not later than Saturday, May 22, 1915.

## NOTES AND QUERIES.

Block Gambier.—Motor Oil.—Can any correspondent (through the medium of your valued publication) give me a method for determining the moisture in block gambier, and does it decompose at, say, 105° C.? Also, at what temperature the viscosity of cylinder oil for petrol motor cars is usually taken by the Sur B. Redwood test?—FARCY W. WESTON.

## MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Royal Society of Arts, 8 (Cantor Lecture). "Food stuffs," by David Sommerville, B.A., M.D.
- TUESDAY, 18th.—Royal Institution, 3. "Advances in the Study of Radio-active Bodies," by Prof. F. Soddy, F.R.S.
- WEDNESDAY, 19th.—Microscopical, 8. "The Male Genital Armature of the *D. maptera*," by Dr. Malcolm Burr. Exhibition of Microscopic Aquatic Life.
- THURSDAY, 20th.—Royal Institution, 3. "The Movements and Activities of Plants," by Prof. V. H. Blackman, F.R.S.
- Royal Society. "Corpuscular Radiation Liberated in Vapours by Homogeneous X-radiation," by H. Moore. "Absorption in Lead of  $\gamma$ -Rays emitted by Radium B and Radium C," by H. Richardson. "Application of Interference Methods to the Study of the Origin of certain Spectrum Lines," by T. R. Merton.
- Chemical, 8.30. "New Method of Estimating Bromine and Chlorine in Organic Compounds," by P. W. Robertson. "Contributions to the Study of Acenaphthylene and its Derivatives," by B. Campbell.
- FRIDAY, 21st.—Royal Institution, 9. "Beauty, Design, and Purpose in the Foraminifera," by Edward Heron-Allen.
- SATURDAY, 22nd.—Royal Institution, 3. "Colouring Matters of the Organic World," by Dr. M. O. Forster, F.R.S.

# THE CHEMICAL NEWS.

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## A SERIES OF NEGATIONS.\*

By J. ECHEGARAY,  
President of the Academy of Sciences of Madrid

JUST as in geological evolution there are periods of calm and relative stability, and, following on them, others of great violence, when we may say that the schematic curve of evolution has its tangents nearly perpendicular to the time-axis—as in the transformation of human society there are periods when the established order remains nearly constant, as if society had reached a state of equilibrium, and other periods of great revolutionary agitation when progress is not content to increase slowly, but seems to leap up to reach higher levels—as in literature, the classical epochs, which are also times of equilibrium, are followed by romantic unrest and modernist extravagances—so in physical science stability and equilibrium are followed by volcanic eruptions, revolutionary transformations, and a certain species of scientific modernism.

In the sphere of intellect, as in human society, these epochs of upheaval and violence are preceded by criticism which is always severe towards the past and seeks perfection in the future.

This criticism proceeds by negations. It seeks out the pillars which support the ancient order and tries to undermine them one by one in such a way that if its object were attained the whole edifice would fall in ruins at once.

For some years physics and, in particular, mathematical physics, has been passing through a great crisis. Classical science, that of Galileo, Newton, Laplace, Lagrange, Cauchy, Gauss, Coulon, Ampère, and many others—I am forced to stop, otherwise the list would be interminable—this science, founded almost entirely upon the mechanistic hypothesis, has been, and is still being, subjected to an implacable criticism; on its supposed ruins, total or partial, men of great talent have been forced to raise up a new science, modern science, and after the modern comes modernism.

The criticism to which we refer, though sometimes much exaggerated, is always worthy of study and reflection, and it has formulated, and continues to formulate, a series of negations which does not seem to have yet arrived at its limit, and which goes on indefinitely.

It is this series of negations which we intend to enumerate in the present article, without pretending to pass judgment on them, merely confining ourselves to making some observations upon them in passing.

### I.

The first negation which we meet, the first pillar of the classic edifice which criticism is undermining, is that of action at a distance, or rather instantaneous action at a distance.

In the old system of mechanics, that of Galileo and Newton, force, in a word universal attraction, was superior to time and space. The most minute particles of matter, the smallest grain of sand on the beach, the most insignificant drop of water in the ocean, an atom of the air we breathe, are all in instantaneous communication with all the matter of the universe; so small, so minute a particle attracts the whole sun, the entire mass of Neptune, the uttermost limit of the nebulous distance, and in their turn all these minute particles of matter are attracted by all the astronomical masses. Everything attracts everything else. And the law of attraction is very elementary, very simple, very amenable to mathematical calculation;

the attraction is proportional to the masses and varies inversely as the square of the distances.

But if enthusiasts have said, and still say, "matter attracts matter in accordance with this law," the prudent add "in natural phenomena things behave as if matter attracted matter proportionally to the masses and inversely to the square of the distances. Belief in universal attraction has brought about wonders, and attraction, real or supposed, has served as the basis of all astronomical science. So that this negation, however important it may be for scientific philosophy, does not shake or shatter the grand monument of celestial mechanics. It is sufficient that the facts should justify the formulæ and should agree with them within the limits of approximation necessary for classical science to subsist independently of any philosophical interpretation.

But the negation of action at a distance is accompanied by another, namely, the negation of instantaneous action.

Common sense applied to science agrees with criticism (which has been sometimes accused of pettiness and materialism) when they affirm that a body cannot exert any action at a place where it is not; that a drop of the ocean cannot have any influence on Neptune and attract it across millions of kilometres, and that this attraction could not travel across space with an infinite velocity like a spiritual thing.

It is evident that the defenders of metaphysics will not accept these negations which they regard as clumsy, without opposing them with affirmations which are as incisive as the negations. To an idealist, or to one who is doubtful about the material reality of phenomena, neither action at a distance nor instantaneous action is as absurd or impossible as they appear at first sight. In this article we do not propose to discuss the fundamental points of the question, but only to enumerate the negations. In any case, even if the negations are admitted to be established, they substitute nothing which absolutely satisfies reason, for if it is agreed that the attractive forces of the astronomical world, or gravitation, are transmitted through space step by step, and with a known velocity which would be either that of light or some other velocity, the difficulty is by no means explained; putting it that way only transfers it from the infinitely great to the infinitely small.

If, for example, action at a distance is impossible between the sun and the earth unless there is some intermediate substance, there is the same difficulty in admitting the occurrence of attractions and repulsions between two atoms. Millions of kilometres are as important as millionths of millimetres. Pascal said, if I make no mistake:—"The infinitely small is a mask of the infinitely great; it is the giant disguised as a dwarf."

It seems as if an explanation of this transmission of force could be obtained by admitting the continuity of matter; but this problem of continuity and discontinuity, which is very obscure in its atmosphere of metaphysics, is itself one of the negations of the series which we shall mention.

We can summarise what has gone before in the two following negations:—(i.). Negation of action at a distance. (ii.). Negation of instantaneous action. We may add that neither of these detracts from the reality of classical science, nor destroys its harmony with facts within the limits of approximation to which human science can attain. Amateurs discuss scientific philosophy, but the practical astronomer and the mathematical astronomer by their observations persevere in their celestial mechanics and their action at a distance, at any rate practically instantaneous.

### II.

Whether action at a distance exists or not, and whether it is instantaneous or not, another negation may be added to the other two, which, however, is not of the same importance—the negation, in many cases, of central forces.

\* *Rev. Gen. des Sciences*, 1915, xxvi., No. 4.



In order to apply astronomical theories, suitably adapted, to molecular mechanics, and in particular to apply the mechanical hypothesis in all its purity, many mathematicians, and among others Cauchy, have reduced all the phenomena of physics so that the equations of dynamics can be adapted to systems of material points between which central forces develop astronomical systems in miniature.

But experience has shown that this is a hypothesis which cannot always be admitted to be exact. It occurs to the mind at once that forces exist in Nature which are not central. The action between an electric current and a magnet is certainly not a central force; the magnet tends to turn round the current or the current round the magnet.

When two infinitely small masses are homogeneous and surrounded by a homogeneous medium, in such a way that the straight line which joins the two points is an axis of the system, there is no reason why the force should not be central, and the old argument of the sufficient reason is convincing to the human mind. But if the two centres of action are asymmetrical and the medium in which they are is not somewhat symmetrical, without having recourse to modernism at all, the old theory of mechanics would give resultants which would not coincide with the line of centres.

Thus this negation of central forces has an incontestable power in many cases; hence, Henri Poincaré amongst his admirable works has published a theory of elasticity in which he completely discards central forces, substituting for this hypothesis the fruitful conception known under the name of function of forces. In this his work is fundamentally differentiated from the classical theory of Cauchy and his disciples.

We may then add to the two first this new negation although there is in it nothing revolutionary or dangerous; it unassumingly occupies one place in the general list.

### III.

We will now criticise a concept which dominates all classical science—force.

We cannot see force directly, but we feel it when we exercise a pressure on a body or when we pull. In fact, we are conscious of force though in a vague form, confusing it more or less with energy. Force dominates all classical mechanics, and we are so accustomed to see it represented graphically by a straight line terminated by an arrow that it is not easy for us to separate the abstract idea from its graphical representation.

We see it almost materialised in reality; in the thread or the string when systems are submitted to tension, or in the bar when they are compressed, or in the different pieces of an iron armature. Even in electricity Faraday imagined tubes of force, and we constantly speak of lines of force and determine their equations.

However, certain critics consider force as a pure idealism, rather as a pure abstraction, and they do not need more to increase the series of negations of modern philosophy by one more negation.

Force they say is not a reality; it must be replaced by a true reality which is energy; from this has resulted the modern theory of energetics, with its youthful ambitions and its inconsistencies as they may be called with all due respect. Strictly speaking, force can be an abstraction; it is useless to deny it, but that is not sufficient to destroy this pillar upon which classical mechanics is so solidly based. For science and even popular opinion are founded on abstractions. Must the mathematical point be rejected because it is an abstraction when compared with the line? Must the line be depreciated because it is an abstraction in comparison with the surface or the surface in comparison with the volume? Abstraction in science signifies neither nullity nor negation. It is only that human intelligence cannot penetrate into the absolute nor encompass it as it would like to; it has to concentrate itself in the finite, and in order to attain the finite it must proceed by a series of abstractions. If force is an

abstraction in comparison with energy a dimension of mechanical energy (if such a comparison is valid), why should not energy also be an abstraction in comparison with more comprehensive realities of a higher order? But we had better pause on this road which would inevitably lead us to the domain of metaphysics.

To return to practical matters, we may say that force, like any other physical concept, as soon as it can be measured passing from a *quality* to a *quantity*, can also be expressed numerically like any concept of quantity, and can enter into mathematical formulæ and take a place in theoretical and in experimental science, and in their calculations from the simplest to the most complicated. When this stage has been reached it is not easy to make an abstraction of it either in classical or modern science. Thus even in the most modern theories force constantly appears with its direction, its magnitude, and its characteristic arrow, and with the mathematical formulæ of its components.

But in the evolution, or we may call it the crisis, of the old mechanics and mathematical physics, if up to the present it has exerted an undisputable hegemony, this is now challenged by a new comer which aims at universal sway, overruling force if not annihilating it. We allude to the concept of energy. One might almost say that force itself has created this powerful rival by creating mechanical work which is a form of energy, and by creating in dynamics kinetic energy or living force. Then energetics has peopled nature with many other forms of energy, but this is a question into which we cannot enter. It is certain that the concept of energy is now dominant in modern theories, especially in electrical and magnetic theories, and that it does what cannot be done by the force of the old theory of mechanics.

But any domination, even if legitimate, can be transformed by abuse into a fatal tyranny, and we cannot see how any new theory can make an abstraction of the concept of force, which for the present prevails in the whole of statics, *i.e.*, in all fundamental problems of equilibrium, although they may be abstract problems and never attain to positive and absolute reality. Force also dominates the dynamics of ponderable masses which is celestial mechanics, and it is frequently resorted to in the newest theories of electricity and magnetism.

Thus in the series of negations which we are enumerating we possess one more semi-negation which is in the same case as the preceding negations; it does not and cannot represent the partial overthrow of the old scientific theory but rather its transformation or extension. Science in its advancement does not proceed by destruction, but raises new erections which enlarge and complete its venerable edifice.

(To be continued).

## THE USE OF RADIO-ACTIVE SUBSTANCES AS FERTILISERS.\*

By WILLIAM H. ROSS,  
Scientist in Soil Laboratory Investigations.

(Concluded from p. 235).

### Composition of Radio-active Manure.

THE source of the so-called radio-active manures consists of the residual rock from which carnotite or other uranium ores have been extracted, or of uranium ores which contain too low a percentage of uranium to make it profitable to extract the radium. Since an ore containing as low as 2 per cent of uranium oxide can be profitably used in the manufacture of radium, it is not to be expected that this percentage of uranium, or its equivalent of radium, will be found in any radio-active manure.

\* Bulletin 149, U.S. Department of Agriculture, Bureau of Soils.

In the following table is given the composition of samples of radio-active materials which have been applied as a manure.

*Analyses of Samples of Radio-active Manure.*

Constituent.	A.	B.
Silica, SiO <sub>2</sub> .. .. .	80.44	85.90
Oxide of iron and alumina, Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .. .. .	2.20	3.65
Lime, CaO .. .. .	—	0.91
Magnesia, MgO .. .. .	—	0.95
Soda, Na <sub>2</sub> O .. .. .	—	0.50
Potash, K <sub>2</sub> O .. .. .	—	1.04
Sulphide, S .. .. .	—	0.16
"Sulphuric acid" .. .. .	5.40	—
Phosphoric anhydride, P <sub>2</sub> O <sub>5</sub> .. .. .	—	Trace
"Soluble phosphoric acid" .. .. .	1.37	—
"Water, volatile organic matter" .. .. .	10.54	0.93
"Soluble salts, soluble free acids" .. .. .	3.32	—
Uranium, U .. .. .	Trace	1.00
Activity .. .. .	0.03U	0.037U

A. — Radio-active manure. Analysis according to Foulkes, *Bul. Bureau Agricultural Intelligence and of Plant Diseases*, iii., 1112. This apparently represents ore from which the uranium has been extracted. The acidity of the material was equivalent to 65 grms. of sulphuric acid per kgm.

B. — Radio-active manure. Analysis by Author. This material represented the original ore, and therefore did not contain any free acid.

*Field Tests with Radio-active Manure.*

Field tests with radio-active manure (A in table) have been made by Foulkes in England (*Bul. Bureau of Agricultural Intelligence and of Plant Diseases*, 1912, iii., 1111). The material used contained only a trace of uranium, but had an activity equal to 0.03 times that of uranium. This was mixed with commercial fertilisers in the following proportions:—Steamed bone, 20 parts; superphosphate, 15 parts; kainit, 10 parts; nitrate of soda, 5 parts, and radio-active manure, 1 part. One plot received an application of this mixture at the rate of 1020 pounds per acre, and an adjoining plot received the same application but without the radio-active manure. Both plots were planted to turnips, and when the crop was grown it was found that the yield was greatest in the plot to which the complete fertiliser, plus the radio-active manure, had been added. A similar result was obtained with mangolds.

Radio-active material of exactly the same composition as that given by Foulkes was also used by Malpeaux in making pot and field experiments with oats, potatoes, sugar beets, and mangolds. (*Vis Agr. et Rurale*, 1913, ii., 241). The material was mixed with a complete fertiliser made up of sodium nitrate, superphosphate, and potassium sulphate to the extent of 5 per cent, and applied at the rate of 22 to 44 pounds per acre. In the case of oats, sugar beets, and mangolds an increased yield of about 15 per cent was obtained on an average on the plots to which complete fertiliser plus radio-active material was added, over that obtained from the plots to which complete fertiliser only was added. In the case of potatoes it was not observed that the radio-active material had any beneficial effect.

A very extensive series of experiments was also carried out by Berthault, Bretigniere, and Berthault (*Ann. Ecole Nat. Agr. Grignon*, 1912, iii., 1), using material for which exactly the same analysis was given as for the radio-active manure used by Foulkes and by Malpeaux. Its effect on a large number of crops (cereals, grasses, and roots) was tested by applying the material alone and when mixed with standard fertilisers. It was found that when the radio-active manure was used alone the positive and negative results were about equal for the total weight of

the plants and for stalks and grain, but the negative results were the more numerous for tubers; with superphosphate the results obtained were generally unfavourable, particularly for the grain, but for tubers they were more often favourable, and with complete fertiliser the favourable results were the more numerous for all crops.

It was concluded that while the results obtained were not decisive they show that radio-active substances were more efficacious in the presence of a complete fertiliser than when used alone or with phosphate or nitrogenous manures.

It is difficult, however, to understand how this conclusion regarding radio-active substances follows from the experiments described by the authors in view of the fact that they acknowledge having had the material which they used tested for radio-activity, and that none could be detected. It therefore follows that the results obtained, whether of a favourable or unfavourable nature, could not have been due to the radio-activity of the material, but to some other influence.

As shown in the table, the acidity of the material was equivalent to 65 grms. of sulphuric acid per kilo., while the "soluble phosphoric acid" amounted to 1.37 per cent and the "soluble salts, soluble free acids" amounted to 3.32 per cent. All these constituents, when exceeding a certain minimum concentration, have a marked effect on plant growth. Notwithstanding this, however, apparently no account was taken of the presence of these constituents in any of the foregoing experiments, but rather all effects observed, whether of a stimulating or retarding nature, were attributed to the exceedingly weak radio-activity of the material, which was claimed to be equal to 0.03 of the activity of uranium, but which, at least in the case of the material used by Berthault, Bretigniere, and Berthault, was too small to be detected.

If it is assumed that the material used in these investigations has the radio-activity which was claimed for it, and that this was due to radium and its products, then it can be calculated that in an application of 25 pounds of the material per acre the amount of radium thus applied to an acre would be less than 1-rootth of the radium already present on an average in an acre-foot of soil. This amount is so small that when uniformly distributed through the first six inches of the soil there would be radiated per second from the material added only about two particles—that is, two atoms—from each pound of soil. Furthermore, of the particles so radiated only a very small fraction would be able to escape from the particles of material in which they originate. The number of  $\beta$  particles radiated would be still less than the  $\alpha$  particles.

The radio-active material (B), of which an analysis is given in the table and which was kindly supplied by a firm in this country, has an activity of 0.037, that of uranium, and is therefore slightly more active than the material referred to above. An application of from 20 to 25 pounds per acre was recommended, mixed with some standard fertiliser, but even in the case where the largest application is used the quantity of radium so applied per acre is only one-fiftieth of the radium already present in an acre-foot of soil. In defence of the use of such a minute quantity of any substance it has been explained that "this material is not a fertiliser, but that it gives to the plant additional power to consume the plant food that is already in the ground or that is put there by artificial means in the form of any brand of fertiliser." The use of the word fertiliser in this statement is no doubt intended to mean a plant food. As already pointed out, however, a material does not necessarily have to act as a plant food to be properly called a fertiliser, for this term is also used with reference to any material which when added to the soil brings about an increase in the growth of crops. If radio-active manure really acts in the way described it could then be properly called a fertiliser, and, further, if its function is to give to the plant additional power to consume plant food, its effect should be noticed when added

to the soil alone as well as when mixed with a standard fertiliser.

Field tests with radio-active mineral from still another source have been made by Ewart, Melbourne University (*Journ. Dept. Agr., Victoria*, 1912, x., 477). These tests were made in two different places, in each of which there were selected a series of four plots. In the case of the first series each plot had an area of one third acre. Plot 1 received 50 pounds of superphosphate per acre; plot 2, 50 pounds of superphosphate and 50 pounds of finely ground radio-active mineral per acre; plot 3, 50 pounds of radio-active mineral per acre, and plot 4 was unmanured. The plots used in the second series had an area of approximately one-fourth acre, and the same applications were made in this case as in the first, with the exception that 50-pound portions of the materials were used instead of 50-pound portions. From the yields obtained it was concluded that "there is no evidence to indicate any beneficial action of the radio-active mineral upon the growth and germination of wheat when quantities which could be used in agricultural practice are employed. Any stimulating action which it might exercise when first applied seems, if anything, to be converted into an injurious action when in prolonged contact. There is nothing, therefore, in these results to show that radio-active mineral is of the least benefit to wheat when applied in the same manner as manure."

#### Catalytic Fertilisers.

In addition to the experiments which have been described on the use of the radio-elements as fertilisers, many tests have also been made during the last few years of the action on plants of still other elements which are not recognised as essential to the growth of plants. Among the different elements which have been studied in this way may be mentioned copper, nickel, zinc, and lead. These elements are of rare occurrence in the soil, and are ordinarily recognised as plant poisons, but quite remarkable benefits have been obtained by the application to the soil of a very small quantity of a soluble salt of these elements. Plants so treated are said to have been stimulated, and because of the small amount of the material necessary to produce noticeable results, these compounds when used in this way are spoken of as "catalytic fertilisers."

With a concentration of one part of lead, as lead nitrate, in 965,000 parts of soil, Stoklasa obtained in pot tests with oats (*Avena sativa*) a maximum increase in growth for the grain and straw of 53 per cent over that which took place in the control pot, but on increasing the concentration of the lead only 2.5 times its toxic action became apparent, and a decrease in growth resulted (*Comptes Rendus*, 1913, civl., 153). Similar results were also obtained, as already pointed out, in pot tests with clover, using uranium nitrate. With this compound the maximum stimulation was obtained with a concentration of one part of uranium in 1,310,000 parts of soil, but as the concentration of the uranium was increased its toxic action became manifest, and the crop yield gradually decreased.

A corresponding series of experiments was also made by Loew and his co-workers using salts of both uranium and thorium (*Bul. Coll. Agr., Tokyo Imperial Univ.*, 1902, v., 173; 1904, vi., 144, 161). From the results obtained it was concluded that "uranium and thorium compounds differ widely in their effects on plants, uranium salts being highly poisonous, thorium salts not" (*Ibid.*, vi., 165). It is known that thorium and uranium both give off the same rays and of approximately the same intensity. It would be expected, therefore, if the effects which these elements produce on plants are due to their radio-activity that the effects would be approximately the same for each element. Since this is not the case, and since the results obtained with uranium correspond with those which follow the use of the so-called catalytic fertilisers, it is necessary to conclude that the action of

uranium on plants is due to its chemical properties rather than to its property of being radio-active.

The material (B), of which an analysis is given in the table above, contains 1 per cent of uranium oxide. An application of this material of about 175 pounds per acre would thus give to the first six inches of the soil a concentration of uranium equal to that which Stoklasa found, in the form of the nitrate, gave greatest stimulation to clover plants. An effect would therefore be expected to follow the addition to the soil of finely ground uranium ores, but whether the result will be beneficial or otherwise will depend on the amount applied and the kind of crops grown.

In the various experiments which have been described on the use of radio-active manure no account has apparently been taken of the chemical action of the uranium present, and the conflicting results obtained with radio-active material from different sources are no doubt to be explained by the fact that the radio activity of the material was alone considered, without regard to the presence or absence of uranium or of such non-radio active constituents as soluble salts and free acids.

The subject of catalytic fertilisers is an interesting one and worthy of careful investigation, but the manner in which they are able to influence so effectively the growth of plants is as yet but little understood. Until further knowledge is gained along this line, and particularly until it is demonstrated that the application of such materials to the soil will not lead to their accumulation with injurious results, the use of uranium, or of any of the other heavy metals as a fertiliser in general farming, is not to be recommended.

#### Summary.

Attention is called to a new material which has recently been exploited for use as a fertiliser, and which consists of the residual rock from which uranium has been removed, or of uranium-radium ores of too low grade to be used for the extraction of radium. This material, which is known as "radio-active manure," is claimed by virtue of its activity to have a marked effect on stimulating the growth of plants when mixed with a relatively large amount of standard fertilisers and applied at the rate of 20 to 50 pounds per acre.

When consideration, however, is taken of the facts:— (1) That the greatest quantity of radium which can exist in an ore amounts to only 0.0003 per cent, (2) that the intensity of the radium rays is limited by the quantity of radium present, (3) that all rays, like all chemical substances, must exceed in intensity or concentration a certain limiting value to produce any noticeable results, or any results whatever; (4) that radium costs 120,000 dol. a grm.; and (5) that the activity of radium or any other radio-element can not be increased by any treatment whatsoever, but remains unchanged in whatever state of combination it may exist, it seems incredible that radium or any of its products can have any economical application as a fertiliser in general farming, and still less credible that the so-called radio-active manure has any value as far as its radio-activity is concerned, since the radium already present on an average in an acre-foot of soil is about 100 times greater than is contained in the quantity of radio-active manure commonly recommended for application to an acre.

Many experiments have been made in studying the influence of the radio-elements when freed from their ores on the germination of seeds and the growth of plants, and from the results obtained it is to be expected that in botanical research, and possibly in greenhouse practice, where the results obtained may justify the expense involved, the radio-elements may prove of considerable value, but when consideration is taken of the scarcity of these elements it does not follow from any experiments yet described that such elements can have any practical application as a fertiliser in general farming.

Evidence is given to show that the action of uranium on plants is due to its chemical properties rather than to its

property of being radio-active, and that the conflicting results obtained with radio-active manure from different sources is to be explained largely by the presence of uranium and of such non-radio-active constituents as soluble salts and free acids.

## PHOTOSYNTHESIS IN ORGANIC CHEMISTRY.\*

### INTRODUCTION AND GENERAL CONSIDERATIONS.

By E. PATERNO.

(Concluded from p 232)

### III.

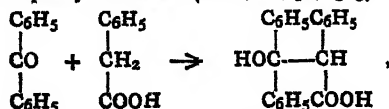
BUT between ketones and aromatic hydrocarbons, under the influence of solar light, a second reaction takes place at the same time, which is perhaps still more general than the preceding; we mean the direct addition of the molecule of the hydrocarbon to that of the ketone with formation of a tertiary alcohol.

Such a reaction has some precedents, not with hydrocarbons but with other organic substances. And first of all Ciamician and Silber (*Gazz. Chim. Ital.*, xlv., [1], 246), extending their experiments of reductions also to an aromatic alcohol, found that benzylic alcohol is added to benzylic aldehyde, thus forming hydrobenzoin, and to benzophenone, giving origin to the triphenylglycol; but they add, as a proof that they had no clear an insight into the reaction, that the very formula of triphenylglycol wanted further experimental proofs in order to be accepted (*Ibid.*, p. 236).

As soon as our experiments were made known, however, Ciamician and Silber hastened to repeat and further extend them.

We had prepared, from toluene and benzophenone, triphenylethanol (*Rend. Acc. Lincei*, 1903, i., 237), from ethylbenzene triphenylpropanol (*Gazz. Chim. Ital.*, xxxix., [2], 421), from propylbenzene triphenylbutanol (*Ibid.*, xxxix., [2], 422), from diphenylmethane tetraphenylethanol (*Ibid.*, xxxix., [2], 427). Ciamician and Silber repeated our experiments with toluene and with ethylbenzene, only finding a few degrees of difference in the melting-points of the products, and they isolated further the product which is formed with *p*-xylene.

This condensation, to which the aromatic nucleus does not participate, but which comes between the carbonyl carbon of ketones and the group CH<sub>2</sub> (mainly), and which we shall call "enolic" for the analogy it has with the aldolic condensation, is not limited to the hydrocarbons or to certain alcohols, but comes about even with derivatives of a different chemical function, provided they contain the group CH<sub>2</sub>. Thus with phenylacetic acid we have obtained triphenyllactic acid (*Ibid.*, xl., [2], 323)—



and with benzylacetate the acetylic derivative of triphenylglycol (*Ibid.*, xl., [2], 331). The enolic condensation we have also studied with the aldehydes. Besides experiments with many paraffin hydrocarbons and benzaldehyde we used benzaldehyde and toluene, dibenzil, diphenylmethane; but it seems that benzoic aldehyde cannot give the reaction on account of the facility with which it polymerises in the light. With anisic aldehyde and piperonal it seems better results may be obtained (*Ibid.*, xlv., [1], 157, 161). Ciamician and Silber obtained important results on extending this reaction to the fatty series, and showing the formation of isobutylenic glycol and of trimethylethylenic glycol from acetone and alcohols (*Ibid.*, xlv., [1], 157).

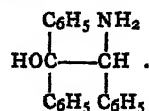
The enolic reaction does not take place with the CO of urea and its derivatives (*Ibid.*, xlv., [1], 162), or with the CO of the amides (*Ibid.*, xlv., [1], 246).

### IV.

BUT with other compounds, besides the hydrocarbons, acids, and some ethers, enolic condensation opens a large field to important researches. I speak of the behaviour of the ketones with bases.

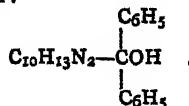
Paratoluidine does not react with acetophenone; methylaniline, on the contrary, gives, as it seems, a product of addition, and with benzophenone a base, certainly of much interest, but whose constitution we have not yet been able to explain.

Benzylamine, which contains the group CH<sub>2</sub>, gives, on the contrary, with benzophenone the enolic transformation very sharply (*Gazz. Chim. Ital.*, xlv., [1], 246), evidently giving origin to the compound:—



Collidine (trimethylpyridine) also gives a product of addition.

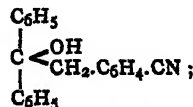
But the subject acquires a greater interest by the study of the vegetable alkaloids. Nicotine with benzophenone gives the enolic reaction, and we have thus a new alkaloid of the constitution:—



Sparteine behaves similarly with acetophenone and benzophenone, forming some products whose study is not yet finished, but which show very typical colloidal properties.

Also important, though in a different sense, are the results we have obtained with strychnine and narceine, and for which we refer to the special paper (*Gazz. Chim. Ital.*, xlv., [2], 99), at the same time pointing to the characteristics of the derivative obtained from strychnine.

In the field of nitrogenous substances we examined also the behaviour of nitriles. As we have had occasion to say, benzonitrile does not react with the ketones, but positive results are obtained with *p*-toluonitrile; a product of addition is formed with benzophenone, evidently of the structure:—



with the meta-compound the reaction is more delayed and the ortho-compound seems not to react.

### V.

BUT beyond the reactions we have illustrated, viz., the trimethylenic, the enolic, and that of the formation of the double hydrocarbons, hydrocarbons and some of their derivatives can react in still another way with the ketones. With this fourth reaction, too, which takes place chiefly with paraffins and substances of the aliphatic series, we have dealt in the preliminary paper of February, 1909; but we have not succeeded in defining it in such a precise manner as we have done with the others.

It is well to premise that Ciamician and Silber, who have often insisted on the fact that the transformation of benzophenone into pinakone, by the action of alcohol, is complete and that benzophenone is completely reduced to benzopinakone (*Rend. Acc. Lincei*, 1901, i., 98; 1911, i., 724), perceived later that in the reduction of benzo-

\* From the *Gazzetta Chimica Italiana*, 1909-1914.

phenone with ether a part of the benzophenone escaped the main reaction, and in May, 1911, they found the fact, *worthy of being remarked*, that ether gives with benzophenone a product of addition (*Ibid.*, 1911, i., 724), when we, since October, 1908, had announced the study of this reaction and the result obtained (*Gazz. Chim. Ital.*, 1909, [1], 237; (*Rend. Acc. Lincei*, 1909, i., 104).

But whatever may be of that, the researches made by us on the reduction of benzophenone with pentane, octane, and decane have persuaded us, on the one hand, that in this instance the hydrocarbon is not doubled, as with toluene and its homologues, and, on the other hand, that the enolic reaction does not take place; we think that in the reaction a less hydrogenated hydrocarbon is formed, but we have not succeeded in isolating it, and have only proved with qualitative tests the probable existence of a hydrocarbon with double links; but the main product besides the benzopinakone is constantly a resinous viscous and transparent substance; these resins for composition and molecular weights approach the compounds of addition of benzophenone with the hydrocarbon.

Having before us, however, the formation of benzopinakone, which, with notable constancy, corresponds to two-thirds of the weight of the ketone used, and the evidence for the presence of an olefine in the recovered hydrocarbon, the most probable hypothesis seems to be that the reaction takes place according to the following scheme:—



In other terms, a molecule of paraffin transforms two-thirds of the benzophenone to pinakone, while it converts itself into a molecule of the corresponding olefine; this is added to the other third of benzophenone, forming an oxytrimethylenic compound.

And we cannot be surprised if with pentane the compound that we have obtained with amylene and benzophenone is not formed, because the amylene that we used was trimethylethylene, while the pentane was the normal one.

Cyclic hydrocarbons, too, that is cyclohexane and its methylic and dimethylic derivatives, give this reaction (*Gazz. Chim. Ital.*, xxxix, [2], 420), hence we may assume that the resistance to this reaction of the hydrogen of benzene is not extended to the more hydrogenated cyclical compounds.

Reactions similar to those of the paraffins and cyclohexane are given by the oxides of alcoholic radicals, acetal and other ethers (*Ibid.*, xl., [2], 327). To experiments in this direction we have referred in the paper of February 7, 1909, and in the Introduction to these studies of October, 1908 (*Ibid.*, 1909, [1], 237), and with more details we made them known in the Nos. III. and IV. of the year 1910 of the *Gazzetta Chimica* published November 14, 1910; but that did not prevent Ciamician and Silber, in the meeting of May 21, 1911, at the Lincei Academy, and with the date of May 22 in the *Berichte* of Berlin, that is a long time after, from dealing with the same argument, as repetition of preceding experiments without caring to make our name and without perceiving that their experiments were repetitions of ours and not a continuation of theirs.

Besides it is a notable fact that Ciamician and Silber in the reaction between benzophenone and ethyl oxide admit that the compound has been formed through the enolic reaction, after which remains to be explained the origin of the hydrogen which transforms the benzophenone to pinakone, which also is formed in great quantities; we, on the contrary, have admitted for this compound the structure of an oxytrimethylenic derivative, and we do not think it necessary to change our opinion. We should not have insisted, perhaps, on this really incomprehensible forgetfulness of Ciamician and Silber, if they had not found us in fault (*Rend. Acc. Lincei*, June 6, 1914) of having forgotten to name them in a *brief note* that we made of the reaction between benzophenone and benzoic aldehyde.

We could say to our justification that we have not made the study of the reaction, so that they have reproached us that not even have we analysed the product, while we have only said it seemed to us *probable* that the polymeride of the benzoic aldehyde described by Mascarelli was formed. And if we have in the hurry made a mistake, which still remains to be proved, it is not all our fault.

Ard Ciamician and Silber, indeed, from the action of alcohol on benzaldehyde have at first obtained a white powder at 100° to 101°, which they have considered as having the quadruple formula of the hydrobenzoin,  $4(\text{C}_{14}\text{H}_{14}\text{O}_4)$  (*Ibid.*, 1901, i., 99), very close, we add, to that of a polymeride of eight times benzoic aldehyde. Later, from the benzaldehyde alone they have obtained a white dusty product melting at 125° to 130°, of the composition, and of the molecular weight nine times the benzoic aldehyde, and which they have declared to be probably identical with the former (*Ibid.*, 1903, i., 336); later still, they have found that the crystallised trimeride of Mascarelli melting at 245° to 246°, was also formed in small quantity, but with it always, and as the main product, the resin that was at first fusible at 100° to 101°, afterwards at 125° to 130°, and now at 160° to 170°, and which, considered at first a polymeride between eight or nine times the benzaldehyde, is now at last acknowledged as a tetrameride (*Ibid.*, 1909, i., 215).

Now it is evident that, not willing to enter into an argument so fruitful of results, we had confined ourselves to a hint corrected by the word "probably." At any rate we wait for the confirmation of the formation in this reaction of the compound of a molecule of benzophenone with two of benzoic aldehyde, which we hope will be soon given us by Ciamician and Silber.

We must once more remember that the synthetical reactions under the action of the light which we have developed in a series of papers published during a period of six years must be considered as acquired from the date of the first paper that we have called the Introduction; we do not wish by saying this to reproach Ciamician and Silber if, preoccupied only with the reducing properties of the alcohols and with the formation of aldehydic compounds from them, they may have in the beginning allowed some more important observations to escape them, and, as they afterwards came to the knowledge of our results, before waiting for the publication of the single experiments, they sought to draw profit from them. But it is also evident that being willing to discuss with us about priority it is necessary to consider at least dates previous to February, 1909. With bibliographical researches made with the greatest care that we are capable of, we have tried to give to each one his own, and we are disposed to correct any forgetfulness that will be shown to us and the faults which we may have fallen into, but we will not allow, at least this time, that others try with artifice to present our work under a false light.

## VI.

Independently of the researches that have conducted us to the general reactions that we have illustrated, we must draw the attention of the chemists to other facts.

1. The study of the numerous synthetical resins that we have obtained gives secure hope that they can serve also to explain the formation and the constitution of some natural resins.

2. The colloidal substances with so characteristic properties obtained from sparteine and from strychnine introduce important facts.

3. The transformation of pyrone into a carbohydrate so like the pentosans deserves attentive study.

4. The formation of organic nitrogenous substances, though of a very indefinite nature, by the reduction of nitrates by the light in the presence of organic substances, can become a field of fruitful researches.

5. The synthesis of photoacetophenine and of its analogues, once better cleared up, may lead to new and more ample researches.



6. The possibility of introducing complex side-chains into vegetable alkaloids of great physiological activity may have some pharmacological applications not without importance.

# VII.

Let us hope that we have succeeded, with this resuming paper, to show that we have filled with a sufficient number of experiments the results announced since our first publication.

I do not expect to continue these studies, but I do not mean with that to preclude the possibility of my completing some arguments and explaining further some others.

## CAMPHOR : NATURAL AND SYNTHETIC.\*

By PERCY A. HOUSEMAN, Ph.D., F.I.C.

CAMPHOR has acquired a special interest within the last ten or twelve years on account of its synthesis on a commercial scale. It represents a good example of a growing tendency to replace natural products by artificially prepared substances, which are either identical in properties with the materials occurring in nature or can be profitably used as substitutes for them. The commercial synthesis of india rubber presents a similar problem which has yet to be solved.

### Natural Camphor.

Natural camphor has been known and prized for many hundred years. The camphor tree (*Cinnamomum camphora*) belongs to the laurel family, and is indigenous to China, Japan, and Formosa. The substance known as Borneo camphor is closely related to the true camphor. Its chemical name is borneol, and it is obtained from *Dryobalanops aromatica*, which grows chiefly in Borneo and Sumatra. Borneo camphor commands a much higher price than Japanese camphor. It is used by the natives for ritualistic and medicinal purposes. Camphor is also obtained from an evergreen semi-shrub (*Blumea balsamifera*) which is found in Eastern India and Burma, and which yields the so-called "Ngai camphor." Within recent years many attempts have been made to cultivate the camphor tree in other countries.

(NOTE.—See, e.g., *Board of Trade Journal*, July, 1907, "Camphor Trees in Federated Malay States"; B. J. Eaton, *Agric. Bull.* Straits Settlements and Federated Malay States, 1909; Colonial Office Report, 1907, No. 527, "Camphor Trees in Ceylon"; Battandier, *Journ. Pharm. Chem.*, 1907, 182, "Camphor Trees in Algeria"; *Chemist and Druggist*, 1907, 109, "Camphor Trees in the United States"; "Camphor Industry in Foreign Countries," U.S. Department of Commerce and Labour, 1910).

These experiments, however, are somewhat hazardous, for though the tree thrives well in almost any sub-tropical climate, and appears not specially subject to attack by insect enemies, about fifty years must elapse before good yields of camphor are obtainable. Individual trees show great variability in the amount of camphor they yield, a phenomenon the cause of which is not well understood.

The question then naturally arises as to the extent of the camphor forests now existing. Until recent years no attempts were made to plant young trees in place of those cut down, but this wasteful policy has now been checked, especially since the Japanese assumed control of the camphor industry after the Chino-Japanese war of 1894.

Between the years 1900 and 1906 some 3,000,000 trees were planted by the Japanese monopoly, and, with the old trees assuring a sufficient supply of camphor for at least fifty years, there is no immediate prospect of a shortage in the supply of natural camphor. The competition which natural camphor encounters with the synthetic article will be treated of later.

\* *Chemical Engineer*, xxi., No. 2.

The following table (*Dis Chem. Ind.*, xxxvi., 355) shows the value (in dols.) of the camphor (presumably crude and refined) exported from Japan and Formosa for the year 1911-1912 (the figures should be accepted with reserve):—

Destination.	1911.	1912.
Hongkong .. ..	15,438	10,956
British India .. ..	285,500	322,000
Straits Settlements ..	4,034	4,900
England .. ..	327,700	362,000
France .. ..	398,000	251,500
Germany .. ..	260,000	244,500
United States .. ..	358,000	228,500
Canada .. ..	6,000	10,400
Australia .. ..	47,000	37,850
Other countries .. ..	24,000	57,800
Totals .. ..	1,725,672	1,530,406

The camphor output of Japan during 1911 was larger than at any time since 1902, over 2,640,000 lbs. having been produced, of which 860,000 lbs. were exported, 1,254,000 lbs. taken by local refineries, 460,000 lbs. by Japanese celluloid factories, the remainder going to general consumers (*Daily Consular and Trade Reports*, No. 229, 15th year, Sept. 28, 1912).

The imports of crude natural camphor from all sources into the United States for the fiscal year ending June 30, 1911, amounted to 3,726,319 lbs., valued at 1,118,586 dols. For 1912 the amount was 2,154,646 lbs., valued at 682,669 dols. (*Ibid.*, No. 261, 15th year, Nov. 5, 1912).

China produces less camphor than Japan and Formosa. In 1912 China exported 105 tons, valued at 130,521 dols., and in 1913 124 tons, valued at 94,298 dols. (*Ibid.*, No. 262, 17th year, Nov. 7, 1914).

The world's production of camphor for 1913 (*Ibid.*, No. 75, 16th year, April 1, 1913) is estimated at about 12,000,000 lbs., of which 4,600,000 lbs. are credited to Formosa, 2,000,000 lbs. to Japan, and 1,300,000 lbs. to China, the remaining 4,000,000 being left for natural camphor produced in other countries and for synthetic camphor.

(NOTE.—All of the statistics are given as they appear in the original sources of information. In some cases these statistics seem to be contradictory—possibly owing to a lack of clearness in separating figures applying to crude camphor from those applying to the refined article).

### Extraction and Refining.

The extraction of the crude camphor from the tree is a simple process. The wood is cut into chips and subjected to the action of steam in stills of primitive construction. The number of camphor stoves in Formosa in 1910 is given as 7834, and the number of camphor workers on the island as nearly 30,000 ("Camphor Industry in Foreign Countries," *Special Consular Reports*, 1910, xliii., Part 3). Formosa supplies about one-half of the total crude camphor produced. Camphor is obtainable from all parts of the tree—leaves, twigs, wood, and roots (see, e.g., B. J. Eaton, *Agric. Bull.* Straits Settlements and Federated Malay States, 1909; Beile and Lemaire, *Bull. Soc. Pharm.*, Bordeaux, liii., 521; *Daily Consular and Trade Reports*, No. 255, 16th year, Oct. 31, 1913).

The crude camphor is divided into three grades, A, B, and BB, and is refined by steam distillation, sublimation, or crystallisation. Refined camphor comes into the market as "flowers," "bells," or "blocks." Camphor oil is obtained as a by-product in the extraction of camphor. The oil is used in perfumery, soaps, &c., and contains many essential oils as well as some dissolved camphor.

### Properties and Uses.

Camphor is a colourless crystalline substance melting at 175° C. It is volatile at ordinary temperature, and its characteristic odour is said to be detectable at a dilution of 0.00005 grm. camphor in 1 litre of air. One part of

camphor requires about 1000 parts of cold water for solution. It dissolves in organic solvents with ease.

Japanese camphor has a strongly dextrorotatory action on the plane of polarised light,  $\alpha_D = 44.2^\circ$  in alcoholic solution. The laevorotatory camphor occurs in the oil of *Matricaria parthenum*, and is known as Matricaria camphor. It is identical with Japan camphor, except for its opposite rotatory power.

Camphor finds application chiefly in three directions:—

1. *In Pharmacy.*—Camphor is used in more than thirty different forms. It is anti-spasmodic, a stimulant, cardiac and local anodyne, and is used in fevers, dysmenorrhoea, colic, &c. Camphor is also used as a disinfectant.

2. *In Explosives.*—Camphor is said to exercise a preservative action on blasting gelatin, but only a small quantity is used in the manufacture of explosives.

3. *In Celluloid.*—Celluloid was invented in 1869 by Hyatt in America, while Daniel Spill worked at the same time in England. The process of manufacture, expressed in a few words, consists of the incorporation of camphor with nitro-cellulose and a suitable solvent such as acetone.

The celluloid industry consumes about three-fourths of the total camphor produced, a fact which will be readily understood when one thinks of the enormous number of articles now made of celluloid.

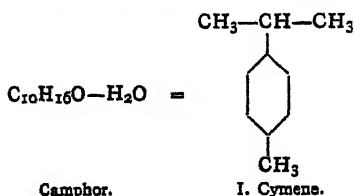
#### Chemical Constitution of Camphor.

This has been a subject of such importance that it is desirable to pass in review the steps leading up to the establishment of the chemical structure of camphor.

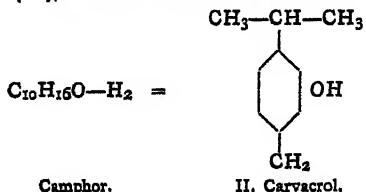
Camphor belongs to the important class of compounds called terpenes, the parent substances of this group being unsaturated hydrocarbons possessing the empirical formula  $C_5H_8$ . The terpenes fall into four classes:—(1) Hemiterpenes,  $C_5H_8$ ; (2) terpenes,  $C_{10}H_{16}$ ; (3) sesquiterpenes,  $C_{15}H_{24}$ ; (4) polyterpenes,  $(C_5H_8)_n$ .

Camphor is a derivative of the second of the above classes, and possesses the formula  $C_{10}H_{16}O$ . It is a saturated compound, and contains the ketonic group  $-C-CO-C-$ , forming a well defined oxime, and yielding a secondary alcohol (borneol) by reduction electrolytically or with sodium amalgam.

When camphor is distilled with phosphorus pentoxide the hydrocarbon cymene (I.) is obtained. Cymene is para-methyl-isopropyl-benzene, and the same complex is therefore assumed to be present in camphor.



On boiling with iodine, camphor is converted to carvacrol (II.), another substance of known structure.



The reactions of camphor considered above are satisfied by the Formula III. proposed by Kekulé in 1873. This formula, however, does not account for the saturated character of camphor, nor for its oxidation to camphoronic acid.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, May 6, 1915.

Sir ALFRED KEMPE, Vice-President and Treasurer, in the Chair.

PAPERS were read as follows:—

"Some Problems Illustrating the Forms of Nebulae." By G. W. WALKER, F.R.S.

The paper is concerned with the form of the surfaces of equal density when a quantity of gaseous material at uniform temperature, and following Boyle's law as regards pressure and density, is at rest under its own gravitation. The differential equation for these surfaces is not linear. In the two-dimensional case Pockels obtained the solution in terms of two arbitrary functions of complex variables.

In the paper the solution is put in a form which must give real positive density anywhere. A solution is—

$$\rho = \rho_1 \left\{ \left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial y} \right)^2 \right\} (\phi^2 + \psi^2 + 1)^{-2};$$

where  $\rho_1$  is a determinate constant and  $\phi$  and  $\psi$  are any conjugate functions of the co-ordinates  $x$ ,  $y$ , such that  $\phi + i\psi = f(x + iy)$ .

Three cases only are considered which illustrate respectively a ring nebula, a pear-shaped nebula, and a nebula with two equal nuclei. It is a matter of detail to examine other cases.

Some consequences of motion of the material are considered.

"Observations on the Resonance Radiation of Sodium Vapour." By Hon. R. J. STRUTT, F.R.S.

1. The centres emitting resonance radiation of sodium vapour excited by the D lines are not persistent enough to be carried along when the vapour is distilled away from the place of excitation. This result is extraordinary, because it contrasts absolutely with the behaviour of sodium vapour excited electrically. It also contrasts absolutely with the behaviour of mercury vapour, whether excited optically (2536 resonance radiation) or electrically.

2. The resonance radiation of sodium cannot be seen through even a very dilute layer of sodium vapour placed in front of it—a layer quite transparent to white light. This explains why the spot of superficial resonance produced on the wall of a glass bulb can only be seen from in front, when the light passes to the eye without traversing sodium vapour. From the back it cannot be seen, as Dunoyer has observed.

3. The resonance radiation of sodium vapour is changed in intensity when the vapour is placed in a magnetic field. If the exciting flame is weakly salted the radiation diminishes with increasing field strength. If the exciting flame is strongly salted the radiation increases to a maximum and then diminishes again.

4. A change in intensity of resonance radiation can also be observed when the exciting flame is placed in the magnetic field. In this case a weak flame gives diminished radiation in the field, while a strong flame gives increased radiation in the field.

5. All the facts summarised under 3 and 4 can be explained qualitatively and quantitatively, so far as the available data will go, by taking into account the known Zeeman resolution of the D lines, and the observed width and structure of these lines as emitted by the flames used. The latter data were obtained by observation with a concave grating of high resolution.

"Local Differences of Pressure near an Obstacle in Oscillating Water." By HERTHA AYRTON.

When the water is approaching the mean level there is a diminution of pressure, or partial vacuum, created in the lee of the obstacle.

When the water is departing from the mean level the diminution of pressure continues high up on the lee side, but over the lower part there is a pressure in the opposite direction to that of the main stream.

The jet in the first part of a swing is due to the local current created by the local difference of pressure; the vortex in the second part of the swing is due to the conjunction of the main stream with the opposing local current set up by the local pressure difference.

# SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 5, 1915.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

The following were elected members of the Society:—

*As Honorary Members.*—Sir William Crookes and Prof. Meldola.

*As Ordinary Members.*—Messrs. Paul Seidelin Arup, Francis Howard Carr, Alexander Scott Dodd, and Harri Heap.

Certificates were read for the first time in favour of—Prof. Arthur William Crossley, Mr. Daniel James Davies, Dr. Martin Onslow Forster, Prof. Herbert Jackson, Mr. Frederic Ion Richardson, Prof. William Jackson Pope, Prof. James Charles Philip, and Mr. George Henry Warburton.

The Ordinary Meeting was followed by a Joint Meeting of the Society of Public Analysts and Other Analytical Chemists and the Biochemical Society; Mr. A. CHASTON CHAPMAN, representing both Societies, in the Chair.

The Meeting was devoted to a discussion on:—

*"Methods adopted in the Estimation of the Nitrogenous Constituents of Extracts derived from Albuminous Substances, such as Meat Extracts and similar products, with special reference to the interpretation of the results."*

The discussion was opened by the Chairman (Mr. CHAPMAN), who drew attention to the necessity of dividing the products of protein hydrolysis into certain groups or categories for analytical purposes. From the technical point of view, the purposes to be served by such analyses were, firstly, to indicate the general character of the process by which any particular extract had been prepared; secondly, to throw some light on the source of the extract and its genuineness or otherwise; and lastly, to furnish information as to the physiological properties or dietetic value. The bromine method, properly applied, precipitated gelatin, gelatin-peptone, syntonin, albumoses, and peptones, but not creatinine or other meat-bases. Saturation of the solution with zinc sulphate in presence of a little acid might be resorted to for the purpose of separating the albumoses from the peptones, and this process, although its results were not very definite, might be useful in so far as it threw some light on the extent to which the original protein matter had been hydrolysed. Bigelow and Cook in the United States precipitated the albumoses and peptones by means of tannin in the presence of salt, and the albumoses being precipitated by zinc sulphate the peptones were obtained by difference. For the determination of gelatin the ice-water-alcohol method of Stutzer was perhaps the most used and most generally considered to give the best results, though some inaccuracy might be caused by the fact that substances rich in albumoses yielded an appreciable proportion of their nitrogen by this method. As to the determination of creatine and creatinine, there seemed little to be said from the chemical side, Folin's method having been thoroughly worked out. The use of ammonium salts had been occasionally alleged, but no case of this very crude form of adulteration had come under his notice, though he had met with a sample of extract which on distillation with magnesium oxide yielded a considerable quantity of ammonia, due apparently to

some putrefactive change. The residual nitrogen was often returned as "meat bases," some analysts using for conversion the factor 3.12, originally suggested by Stutzer on the basis of the nitrogen percentage of creatine. Hefner, however, had suggested the use of the ordinary protein factor of 6.25, which at least had the merit of not involving any assumption or giving to the results an apparent accuracy which they did not in fact possess, though, on the other hand, to those who did not understand the matter, the quantity of "meat bases" might be made to appear much larger than it really was, while a considerable error was thrown on the proportion of non-nitrogenous extractives, which was arrived at by difference. The best plan was to return the actual nitrogen percentages.

Prof. F. GOWLAND HOPKINS said that the animal body dealt not with the intact proteins, or even with the albumoses and peptones, but with the free amido-acids which were the individual constituents of the protein molecule. The actual way in which the different amino-acids were grouped in the protein molecule was not of much consequence, but the effects produced by the individual amino-acids were of extreme importance. He described physiological experiments which he had made, showing that when rats were given a diet including a complete amino-acid mixture corresponding to the proteins of an ordinary diet their growth was almost exactly normal, while, when argentine and histidine were removed from the amino-acid mixture the growth ceased immediately, being resumed when argentine and histidine were again added. The removal of tryptophane from the amino-acid mixture also produced similar results, and Osborn and Mendel in America had shown cystine to be similarly essential. It did not follow that this was the case with every amino-acid, and the question as to which of the amino-acids were essential in that way offered a large field for investigation. Recent work at Cambridge indicated that certain acids could be removed from the amino-acid mixture without affecting the rate of growth. With regard to the minimum quantity of any amino-acid required for nutrition, experiment had shown that in the case of rats, at any rate, the critical minimum for argentine lay somewhere between 2½ and 1 per cent. It appeared that the functions of the individual amino-acids were not confined merely to flesh formation. The effect of feeding animals on zein, which was deficient in both tryptophane and lysine, was not only to restrict growth but also to shorten the survival, and the same was observed with zein plus lysine, but with zein plus tryptophane the animal was able to maintain its weight for a long period, although it did not grow. It was clear from this that the tryptophane exercised some other function than the mere supply of material for growth. Further work on this subject is proceeding at Cambridge.

Dr. E. P. CATHCART, referring to creatine and creatinine, said that the observations at present available were so scanty that it could not be said with certainty that creatine and creatinine had a special niche in the organism. Creatinine of course was a constant excretory product, but creatine was not, except in the case of infants, though it might be made to appear if an animal were starved or treated with certain drugs. Folin had stated that creatine was a fairly valuable foodstuff, but he (Dr. Cathcart) did not think on the evidence available that it was. He did not think that any end would be gained by the separate estimation of creatine and creatinine in meat extract, since a large part of the original creatine would probably be converted into creatinine during the process of manufacture.

Mr. A. R. TANKARD thought that it was important in some cases to separately estimate the meat fibre and coagulable albuminoids, with a view to the detection of extraneous matters which were sometimes added. For some time past he had adopted the method of centrifugalising the bromine precipitate, mixing the residue with water, and centrifugalising again. He made a prac-

tice of separating the albumoses and peptones, but agreed that in most ordinary cases this was of little value. There were, however, on the market certain so-called "fortified" meat extracts, which contained albumoses and peptones in very much larger proportion than occurred in ordinary meat extracts. With regard to the factor used for converting the residual nitrogen into "meat bases," he remarked that this was the only instance which he knew of in chemistry in which a factor known to be wrong was used merely for convenience.

Mr. E. HINKS remarked that the use of a factor of approximately 3 for calculating the "meat bases" from the residual nitrogen seemed to be justified by the fact that the proportions of nitrogenous and non-nitrogenous extracts thus obtained were about equal, this being what one would expect in the case of such a product as meat extract.

Dr. PERCIVAL HARTLEY described his experience of Van Slyke's method of determining amino nitrogen, which was based on the fact that when protein and protein degradation products were treated with nitrous acid nitrogen gas was given off. The results of complete analyses of various proteins showed that the constitution of serum albumen was quite different to that of globulins, the former containing a much larger proportion of lysine and of cystine than the latter. Another interesting result was that the globulins exhibited no difference in chemical composition, eu-globulin and pseudo-globulin apparently being closely related. Another point brought out was that the free amino nitrogen of native proteins appeared to be approximately one-half of the lysine content, which if substantiated would appear to afford a simple method of estimating lysine without hydrolysis of the protein. Furthermore, the proportion of free amino nitrogen indicated to what extent the protein had been digested or peptonised.

Further remarks were made by Dr. Rideal, Prof. Barger, Prof. Harden, Dr. G. S. Walpole, Dr. Cathcart, Prof. Gowland Hopkins, and the Chairman.

## THE ALCHEMICAL SOCIETY.

### ALCHEMY AND MYSTICISM.

THE twentieth General Meeting of the Alchemical Society was held on Friday, May 14. The Chair was occupied by the Acting President, Mr. H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

A paper entitled "*The Beginnings of Alchemy*" was read by Mr. ARTHUR EDWARD WAITE, an Honorary Vice-President of the Society and a well-known authority on the subject. He commenced his most interesting lecture by a summary of the early history and literature of alchemy in Europe, then dealt with the Leyden papyrus, the Byzantine alchemists, with special reference to Sosimus and pseudo-Democritus, the Arabian and Syriac alchemists, and the alleged practice of alchemy in China. The lecturer then proceeded to the difficult question as to whether any of the texts, referred to in the earlier part of the lecture, bore a mystical rather than a physical interpretation, and considered the genesis, history, and present position of the mystical or spiritual interpretation of alchemy.

The lecture was followed by an animated discussion, after which the third Annual General Meeting of the Society was held. It is pleasing to note that, in spite of the war, the Society has maintained its activities during the past eight months with but little decrement. Increased support, however, from those interested in the history of science and philosophy, and the development of man's ideas of the universe, is needed, and will, it is hoped, be forthcoming.

A full report of the proceedings, containing the text of the lecture in full, will be published in the May issue of the Society's *Journal*.

## NOTICES OF BOOKS.

*An Amateur's Introduction to Crystallography.* By Sir WILLIAM PHIPSON BEALE, Bart., K.C., M.P. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THIS excellent book is intended for the use of the reader of mature age who has taken up the study of crystallography as a hobby. Such a reader would in all probability have a basis of a good knowledge of mathematics and of the elements of mineralogy, and the book will help him to rub them both up and add to them, and may lead him on to the fascinating study of the optical properties of crystalline substances. The subject is approached from observations of the external form of crystals, made with the naked eye or with the aid of the microscope or goniometer. Very clear illustrations are given, prepared from actual more or less imperfect crystals, and practical methods of measurement are explained. The thirty-two classes of crystals are enumerated and briefly described, and the discussion of the practical occurrence of crystalline forms follows. Actual methods of calculation are described in an appendix, and some hints are given on the drawing of crystals from elements and indices.

*Chemical Technology and Analysis of Oils, Fats, and Waxes.* By Dr. J. LEWKOWITSCH, M.A., F.I.C. Edited by GEORGE H. WARBURTON. Fifth Edition, Vol. III. London: Macmillan and Co., Ltd. 1915.

THIS volume contains detailed accounts with full tables of statistics, &c., of the technology of manufactured oils, fats, and waxes, and the technical and commercial examination of the products of the oil and fat industries. An account is given of the hydrogenation of oils and fats, and recent processes and methods are fully described. The technology of waste oils and fats and of the commercial products derived from them is also treated in the volume, which completes the fifth edition of Dr. Lewkowitsch's comprehensive work.

*The Chemistry of Paints and Painting.* By Sir ARTHUR H. CHURCH, K.C.V.O., F.R.S., M.A., D.Sc., F.S.A. Fourth Edition. London: Seeley Service and Co., Ltd. 1915.

IN the latest edition of this book various corrections have been made and certain parts have been abridged or omitted. On the other hand some paragraphs which appeared for the first time in the German edition of 1908 have been translated and inserted. The book is already well known to artists, to whom it probably needs no recommendation. It gives interesting accounts of the substances they use, including paper, wood, and canvas, as well as paints, and the operations they practise, and some simple practical tests of materials are described. A chapter on the study of old paintings contains some general remarks upon the materials employed and the changes they have undergone in the case of a certain number of pictures in the National Galleries of London, and the chapter on the conservation of pictures and drawings contains a discussion of the selection of glasses, &c., for covering, allusion being made to the possibility of using the eye preserving glasses described by Sir William Crookes.

*Tables Annuelles de Constantes et Données Numeriques, de Chimie, de Physique, et de Technologie.* "Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological". Paris: Gauthier-Villars. Leipzig: Akademische Verlagsgesellschaft. London: J. and A. Churchill. Chicago: University of Chicago Press. 1914.

AN announcement of the publication of the above tables was made in our issue of March 12th. We have now received a series of reprints containing the data connected with the various subjects included in the larger work.

This arrangement will be found in many cases to be a distinct advantage, the small sections are easy for reference and occupy very little space. Six such reprints have been issued containing the data of Volume III.

As is well known these "Numerical Tables" are compiled under the direction of a representative International Committee of leading authorities, gentlemen who have no commercial interest in the work, but without whose assistance such a selection of data would be of little value.

For the convenience of those interested we give the following particulars of the parts now ready:—

- A.—Spectroscopie; L. Brünninghaus. 74 pp. 10 frs.
- B.—Electricité, Magnétisme; Dr. L. Mahlike. Conductibilité des électrolytes; Prof. W. C. McC. Lewis. Forces électromotrices; Prof. P. Dutoit. 79 pp. 10 frs.
- C.—Electronique, Ionisation, Radioactivité; J. Saphores. 9 pp. 2.50 frs.
- D.—Cristallographie et Minéralogie; L. J. Spencer. 19 pp. 4 frs.
- E.—Biologie; L. Terroine. 17 pp. 4 frs.
- F.—Art de l'Ingénieur; G. Fiek, W. Hinrichsen. Métallurgie; S. L. Archbutt, Portevin, Nusbaumer. 74 pp. 10 frs.

## OBITUARY.

D. A. LOUIS, F.I.C.

At a meeting of the Committee of the British International Association of Journalists, Mr. THOMAS CATLING, the President in the Chair, most sympathetic references were made to the loss the Association had suffered by the death of their representative on the Central Committee of the Associations of the Press, Mr. D. A. Louis, the scientific journalist. Mr. Catling especially referred to the value of Mr. Louis' work, and Sir JAMES YOXALL also spoke of the suddenness and sadness of their representative's death and how they would miss his counsels upon international work.

The Honorary Secretary, Mr. JAMES BAKER, read the following short note upon Mr. Louis' life and general journalistic work, and the Committee passed a vote of sympathy and condolence to Mr. Louis' brother.

The British International Association of Journalists has lost by the death of D. A. Louis a most important official, one who has done difficult work for the Association of the highest order—work that required cosmopolitan and linguistic knowledge, and adaptability to the varied idiosyncracies of the men of many countries. Beneath his easy going, genial, light, and seemingly erratic nature, there was a keen fixity of purpose when important work was before him, that carried him straight to the end aimed at, and this fixity of purpose often served us well when difficult and disputed points arose on the Central Bureau or at our own meetings. He saw what policy was of importance for the welfare of the British International Association of Journalists, and with few words impressed his ideas upon those around him and carried his points.

He joined our ranks in 1899, on March 1st, at a general meeting held at Upper Woburn Place, under the presidency of Mr. P. W. Clayden, and on the 15th March his name appears on a Sub-Committee for carrying out the receptions of the Central Bureau; there is no date on the printed document referring to this. On the 21st March, a letter of thanks was sent to Mr. Louis for his assistance during the visit of the Bureau, and on November 2nd, 1900, his name appears on the list of the Committee bracketed as Paris delegate, showing how his polyglottic work was at once recognised and appreciated.

On the 25th of March, 1904, he was elected as our delegate on the Central Bureau, and in 1906 he was re-elected to the position, which he held until his death in 1915.

Whilst he was serving us well in this responsible work, he was doing very remarkable scientific and journalistic work of a very high order.

He travelled on scientific expeditions not only to the ends of the earth, but to difficult spots in the centre of the earth. Referring once to the curious truncated appearance of one of the cones of Mount Ararat, he exclaimed "I've been there," and he quickly proved he knew the district and the Governor of the Caucasus, then Prince Galitzin.

When we were preparing for the International Press Congress in London in 1909, he was suddenly sent on a special mission to explore scientifically the Island of Saghalien, beyond Siberia, but he turned up again as though he had come from Paris only just in time for our Conference.

His knowledge of many scientific matters, especially in chemistry and mining, was very thorough, and the advantage of this knowledge to our Association was illustrated at Vinohrady, near Prague; when a professor was describing in German, the value of inoculation of plants, and Mr. Louis translated this in easily understood English for our members, who were travelling through Bohemia as guests of the people and Government.

In his rooms were always crowds of scientific books in many tongues, that he was reviewing for the scientific journals, and amongst his important journalistic work were his reports of certain sections of the British International Association's annual meetings for the *Times*, *Engineer*, and the chemical journals. He was thorough; and when he had to go to Colorado, on some mining business, he went back to the School of Mines to prepare himself for his work. He had been examiner in mining for the Board of Education, and Professor of Mining at Leeds, and he went into the Egyptian desert to discover petroleum, on which subject he read a paper at a Petroleum Congress at Bucharest. All these expeditions he turned to good account, in his reliable, scientific, journalistic work.

We have lost a good comrade, a good friend, and an important member; who always worked for the elevation and development of the British International Association of Journalists.

The Association was represented at the funeral by Mr. Walter Jerrold and Mr. Leon Gaster.

The Committee unanimously elected Sir James Yoxall, M.P., to take the place of Mr. Louis as their representative on the Central Committee, and Sir JAMES YOXALL expressed the hope that after the war their International work would be resumed with all neutral countries and even with Austria, although there would be difficulties in again building up the friendships of the past.

The Committee voted the sum of 10 guineas for the Emergency Funds for Belgian Journalists, of which the Honourable Harry Lawson, past President of the Institute, is the Chairman.

## CORRESPONDENCE.

### THE CHEMIST'S REWARD.

To the Editor of the Chemical News.

SIR,—After all that has been said and discussed by the Society of Technologists, as reported in the recent issues of the *CHEMICAL NEWS*, it is to be hoped more action and less words will now occur to put the industrial chemist and technologist on a better footing, and be treated as a professional man, and not as a junior clerk, typist, or shorthand writer, as expected. The reward nowadays is meagre enough, but since hostilities began chemical manufacturers pay less, and no doubt they are taking their cue from the recent Government inquiry for chemists at £2 os. 6d. per week. Things are surely come to a crisis when the writer cannot get even £3 a week after over twenty years' varied works experience, and then is expected to do odds and ends irrespective of his profession. —I am, &c.,

PERPLEXED.



## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx. No. 13, March 29, 1915.

**Constitution of Glycerophosphoric Acid of Lecithin.**—O. Bailly.—The existence of monoglycerophosphoric acid in the molecule of the lecithin of eggs was proved for the first time by Gobley in 1846, but it was not known whether it was present in the  $\alpha$ -form,  $\text{PO}_4\text{H}_2\text{CH}_2\text{CHOH}\cdot\text{CH}_2\text{OH}$ , or in the isomeric  $\beta$ -form,  $\text{PO}_4\text{H}_2\text{CH} < \begin{smallmatrix} \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} \end{smallmatrix}$ . By determining the solubility of the calcium salt the author has found that lecithin contains a mixture of at least two isomers; the  $\beta$ -form predominates, while the  $\alpha$ -form is present only in the proportion of about 1 to 4.

No. 14, April 6, 1915.

This number contains no chemical matter.

No. 15, April 12, 1915.

**Hydrate of Arseniuretted Hydrogen.**—M. de Forcrand.—The author prepared arseniuretted hydrogen by the action of cold water upon aluminium arsenide, and then subjected the gas and a few drops of water to progressive compression in a Cailletet's apparatus. Thus crystals were obtained which could be kept indefinitely between  $0^\circ$  and  $28.2^\circ$ , under a minimum pressure which increased with the temperature. Above  $28.2^\circ$ , at  $29^\circ$  for example, the hydrate was destroyed, and could not be again obtained even under pressures of 30 to 40 atmospheres. The formula of the hydrate was found to be  $\text{AsH}_3 + 6\text{H}_2\text{O}$ .

*Bulletin de la Société Chimique de France.*  
Vol. xvii.-xviii., No. 2, 1915.

**Heats of Formation of Acrolein and Metacrolein.**—E. Voisenet.—The heat of formation of acrolein from its elements (C diamond, H gas)  $\text{C}_3 + \text{H}_4 + \text{O} = \text{C}_3\text{H}_4\text{O}$  liq. is 27.48 cal. The dehydration of glycerin is a feebly exothermic reaction. The heat of formation of metacrolein from its elements (C diamond, H gas)  $\text{C}_3 + \text{H}_{12} + \text{O}_3 = \text{C}_3\text{H}_{12}\text{O}_3$  cryst. is 92.65 cal.

## MISCELLANEOUS.

**South African Association for the Advancement of Science.**—The thirteenth Annual Session of this Association will be held at Pretoria from Monday, July 5, to Saturday, July 10, inclusive, under the presidency of Mr. R. T. A. Innes, F.R.A.S., F.R.S.E., Union Astronomer.

## Sectional Committees.

**Section A.**—Astronomy, Mathematics, Physics, Meteorology, Geodesy, Surveying, Engineering, Architecture, and Irrigation.—President: F. E. Kanthack, M.I.C.E., M.I.M.E. Vice-Presidents: G. W. Herdman, M.A., M.I.C.E., and Prof. J. Orr, B.Sc., M.I.C.E. Members: Prof. R. H. Charters, M.I.C.E., Prof. P. G. Gundry, B.Sc., Ph.D., A.R.C.S., Prof. R. A. Lehfeldt, B.A., D.Sc., Prof. A. Ogg, M.A., B.Sc., Ph.D., A. H. Reid, F.R.I.B.A., F.R.San.I., A. W. Roberts, D.Sc., F.R.A.S.,

F.R.S.E., and H. E. Wood, M.Sc., F.R.Met.S. Hon. Secretaries: Prof. A. Brown, M.A., B.Sc., South African College, Cape Town (Recorder), and J. L. Soutter, Arcadia, Pretoria.

**Section B.**—Chemistry, Geology, Metallurgy, Mineralogy, and Geography.—President: H. Kynaston, M.A., F.G.S. Vice-Presidents: E. T. Mellor, D.Sc., F.G.S., and Prof. J. A. Wilkinson, M.A., F.C.S. Members: C. F. Juritz, M.A., D.Sc., F.I.C., Prof. S. J. Shand, D.Sc., Ph.D., F.G.S., Prof. G. H. Stanley, A.R.S.M., M.I.M.E., M.I.M.M., F.I.C., and Prof. R. B. Young, M.A., D.Sc., F.G.S., F.R.S.E. Hon. Secretaries: H. C. J. Tietz, M.A., Ph.D., South African College, Cape Town (Recorder), and Prof. D. F. du Toit Malherbe, M.A., Ph.D., Transvaal University College, Pretoria.

The following papers have already been promised:—

## Section A.—

Presidential Address.

"Fire Resisting Materials in Building Construction"; by A. H. Reid, F.R.I.B.A., F.R.San.I.

An Astronomical paper; by Dr. A. W. Roberts.

## Section B.—

Presidential Address.

"The Intrusions in the Parys Granite"; by Prof. S. J. Shand, Ph.D., D.Sc., F.G.S.

"The Fault System of the South of Africa"; by Prof. E. H. L. Schwarz, A.R.C.S., F.G.S.

"The Mineral Spring on the Farm Rietfontein, District Brandfort, O.F.S."; by Prof. M. Rindl, Ing.D.

"Notes on the Chemistry of the Naras plant (*Acanthosicyos horrida*, Hook)"; by Dr. W. Versfeld and G. F. Britten.

"General considerations affecting Banket Ore Treatment"; by Dr. W. A. Caldecott, B.A., F.C.S.

A paper by Prof. J. A. Wilkinson, M.A., F.C.S.

**Action of Metals on Chlorides of Carbon.**—Enrique V. Zappi.—The author has studied the action of various metals (aluminium, magnesium, &c.) upon  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ ,  $\text{C}_6\text{Cl}_6$ , and  $\text{C}_{10}\text{Cl}_8$ , and has deduced the following conclusions:—1. The carbon, which is obtained by the reduction of  $\text{CCl}_4$  by aluminium, contains at least 12 atoms in the molecule, and the equation  $\text{CCl}_4 + \text{M} = \text{MCl}_4 + \text{C}$  is accompanied by the polymerisation of the carbon formed. 2. The greater the molecular weight of a chloride of carbon, the higher the temperature at which it is decomposed by metals. 3. The ease with which metals attack chlorides of carbon is directly related to the amount of heat produced by the formation of the metallic chlorides.

	Cal.
$2\text{Al} + 3\text{Cl}_2 = \text{Al}_2\text{Cl}_6$ sol.	+ 323,600
$2\text{Fe} + 3\text{Cl}_2 = \text{Fe}_2\text{Cl}_6$ sol.	+ 192,000
$\text{Mg} + \text{Cl}_2 = \text{MgCl}_2$ sol.	+ 151,000
$\text{Si} + 2\text{Cl}_2 = \text{SiCl}_4$ gas	+ 121,800
$\text{Na} + \text{Cl} = \text{NaCl}$ sol.	+ 97,900

—*Anales de la Sociedad Química Argentina*, 1914, ii., No. 8.

## MEETINGS FOR THE WEEK.

TUESDAY, 25th.—Royal Institution, 3 "Colouring Matters of the Organic World," by Dr. M. O. Forster, F.R.S.

FRIDAY, 28th.—Royal Institution, 9. "Engineering Problems of Mesopotamia and Euphrates Valley," by Sir John Jackson, C.V.O., &c.

— Institution of Petroleum Technologists, 8 "Evolution of the Oil Tank Ship," by H. Barringer.

— Physical, 5 "Numerical Relations between Electronic and Atomic Constants," by H. S. Allen. "Method of Calculating the Absorption Coefficients of Homogeneous X-radiation," by H. Moore. "Two Experiments illustrating Novel Properties of the Electron Currents from Hot Metals," by O. W. Richardson. "High Permeability in Iron," by E. Wilson.

SATURDAY, 29th.—Royal Institution, 3 "Mary Queen of Scots," by Prof. R. S. Rait.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2896.

## A SERIES OF NEGATIONS.\*

By J. ECHEGARAY,  
President of the Academy of Sciences of Madrid.

(Concluded from p. 242).

### IV.

CONTINUING our series we arrive at another negation which we should not hesitate to designate formidable if we were not afraid of prematurely exhausting the many adjectives required to express astonishment and stupefaction.

If anything appeared solid and indestructible in the old mechanics it was the concept of mass. Mass was invariable, eternal, indestructible, always the same. It could be subdivided in space, but the sum of its parts was always equal to the original mass. If, choosing suitable units, mass was expressed by a number, this number would be unalterable from century to century; mass was eternal. Without meaning to, we instinctively confused mass with matter in its most essential and permanent property. Mass was quantity of matter, and the more matter there was in it the denser the mass and the greater the number expressing it.

These are tendencies of the mind, the legitimacy of which may be doubtful, but they are natural tendencies which are strengthened every day by the realities of life and even by scientific theories. The whole of chemistry is based upon this postulate, and classical chemistry would fall to the ground if the practical variability of mass were admitted.

Whether a body is motionless or moving, whether it moves slowly or rushes along with the velocity of light, everybody believed that its mass remained unalterable. In a word the mass was independent of the velocity.

Now this categorical affirmation of classical science is opposed, not I may say by criticism, but by an equally categorical negation on the part of modern science, its most fascinating theories, and its leading experimentalists. Mass is not invariable; it is a function of velocity and of the direction of velocity. There is a longitudinal and also a transversal mass, both depending upon velocity; generalising this idea, we are led to believe that there is a distinct mass for each orientation; but the explanation of this point would take us too far.

The position of classical mechanics in the face of such negations and affirmations is truly difficult. Up to the present it had relied upon a unique and constant mass, and suddenly it meets with at least two masses, the longitudinal and the transversal, and both vary with the velocity of motion.

The following is an example, an imaginary experiment, which will, perhaps, enable us to explain the singular concept of variable mass with the concepts of classical mechanics.

Imagine a body M, the mass  $m$  of which we will suppose to have been determined experimentally. Let the body M during a time  $t$ , and in the direction of a straight line along which its centre of gravity will travel, be subjected to a force F, which we can measure, and which we will suppose constant during the same time  $t$ . The experiment consists simply in measuring the velocity  $v$ , which the force has communicated to the body. From the elementary equation  $mv = Ft$  we can deduce the unknown  $m$ , which will be given by  $m = \frac{Ft}{v}$ . Knowing F and  $t$ , and

having measured  $v$  we shall obtain the value of  $m$ . And if we repeat the experiment once, twice, a hundred times we shall always obtain the same value of  $m$ , allowing for the small experimental errors. We have once again proved the constancy of mass, although in the series of experiments F,  $t$ , and  $v$  have varied in the different cases. But suppose that before another experiment was performed an evil spirit united the body M by some subtle spring to an elastic system, a kind of dynamometer, and suppose the dynamometer and the spring were so subtle and so invisible that we could not perceive them, so that we should imagine that in the new experiment the conditions would be the same as before. If the elasticity of this system of springs acted in such a way as to oppose the motion, in measuring the velocity we should get a value  $v'$  less than the preceding, and the new value  $m'$  of the mass would be  $m' = \frac{Ft}{v'}$ , evidently greater than the constant value obtained in the earlier experiments, since  $v'$  is less than  $v$ .

Our astonishment would be justified, if, in agreement with classical science, we believed in the invariability of mass and if we did not know that the experiment had been complicated by the addition of an elastic system.

Something similar has occurred in the case of many of the problems of bygone science, for electrical phenomena have appeared to complicate those of the old ponderable matter, traditional matter which was so simple and obvious.

When a small sphere is in motion with an electric charge, the elastic system of our example is composed of this charge and all the electro-magnetic field which the charge in motion produced in the ether, that is to say, the radial electric field and also the magnetic rings which surround the line of movement. Abraham's dynamics of the electron, and Lorentz's theory of the electrons, which are truly admirable new theories, have had a powerful influence in the creation of the new concept of electro-magnetic masses, varying with the velocity and the orientation; all these theories can be worked out by calculation. At first sight these theories, which have been mostly verified by experiment, diminish the crudity of the original negation because it is not the ponderable mass which changes; but the classical ponderable substance is accompanied by another element, electricity, which if it has not got mass exactly simulates it by movement: mass variable with the velocity, and with the variability of which ponderable matter is in some way an accessory, without being the cause of this apparent overthrow of the classical laws of physics.

It is truly remarkable and worthy of reflection that we can study the movement of the electric fluid, or more concretely the electron; that we can attribute to it a mass which is not concentrated in it as in ponderable bodies, but which is in some way diffused in the ether; finally that electric charges in motion simulate, if the word may be used, masses and inertias which scientific men explain by calculations which are as ingenious as they are bold. But this does not suffice to alter the fixity of one of the great laws of classical science, the invariability of mass. The defenders of tradition in mechanics and mathematical physics might argue thus, endeavouring, in order to weaken the disconcerting negation, to create a sort of *modus vivendi* between invariable ponderable mass, between the matter which surrounds us and to which we are accustomed, and the new law of electricity in motion. But the *modus vivendi* runs risks, and the negation is confirmed and strengthened, as we shall see.

### V.

The hypothesis of the atom, which was till recently nothing but an hypothesis, is nowadays regarded as a reality by almost all physicists, including the illustrious Poincaré, thanks to the admirable experiments of Perrin. The atoms can be counted and measured, and enthusiasts would even say that they can be seen. To-day, however,

when they have proved themselves to be a reality, a terrible negation, one might also say a sentence of death, falls on them. In the mind of physicists and chemists of the old school the atom was the simplest unit, indivisible, incorruptible, eternal. An atom of ponderable matter, an atom of oxygen, hydrogen, or nitrogen, passing through our laboratories came, according to unanimous opinion, from the depths of the past and of space in the form in which it reached us, and left our apparatus to pass to new abysses in the future, remaining always the same. The atom was eternal. The philosophers of the materialist school could call it a god: the god Atom. The invariability of mass, of which we have just been speaking, was explained by the invariability of the atom. And then comes a new negation, or a new series of negations—the atom is not invariable.

Moreover this is not a theory; the complexity of the atom, its decomposition, its disintegration, and its transformations can be seen, followed, and even measured. This is what radio-active substances and the whole theory of radio-activity tell us. It is true that originally radio-active substances were exceptions, but now we regard radio-activity as a general property of matter which is most marked in uranium, radium, and its congeners. Thus from the moment when the classical atom lost its unity and its prestige, and when each atom was regarded as an infinitely small but infinitely complex system, imagination leapt forward, and hypotheses concerning the constitution of these infinitesimal entities have multiplied.

We have Thomson's atom, with its central element of positive electricity in which the negative electrons are, so to speak, stamped in the form of rings; thus by the play of reciprocal attractions and repulsions equilibrium is established; sometimes it is lasting, and then the atom remains invariable, and sometimes it is destroyed, the number of rings and the number of electrons in each ring being invariable (*Phil. Mag.*, No. 39, March, 1904).

A new hypothesis converts the atom into a kind of planetary system, with its positive electron at the centre and its negative electrons not fixed, but revolving round it like planets. Without respect for the mystery of the atom we have increased its complexity, introducing into it a new system of magnetons.

Summarising, the extremely simple atom of the ancient atomic theories has become an electric complex in which all the hypotheses find an application and have distinguished protagonists. Without pretending to study them for the moment, and taking them altogether, we can deduce a powerful tendency to convert the traditional atom of ponderable matter into an electric system of extraordinary complexity: free atoms, rings, currents, magnetons, a whole electric world, without any explicit residue of ponderable matter.

Thus in this new theory ponderable matter disappears; everything is electricity in the universe—the negative electron, the positive electron, the electric current, and magnetism, which on Ampère's hypothesis is converted into a system of currents.

If the *modus vivendi* which we had established above, in order to preserve the invariability of ponderable matter, were what it pretended to be, it would be shattered and annihilated in the most disastrous way for the old matter of classical tradition. It is true that if ponderable matter does not exist as a special substance, essentially distinct from the electric fluid or electric atoms, there is no need to trouble about the invariability of mass of the old mechanics. Strictly speaking it is constant, since being non-existent it is equal to zero—a triumphant conclusion, the constancy of zero, the invariability of nothingness! But if ponderable mass does not exist, and if all mass is electromagnetic, all mass will be essentially variable and will depend upon the velocity. The negation which we have previously mentioned acquires an enormous force, and neither adaptations nor palliatives are any good: mass is essentially variable, and one of the pillars of classical mechanics has completely given way.

## VI.

Thus it appears at first sight, but there is no foundation for the fear. However ponderable matter is regarded, whether it is reduced to a collection of electric systems or not, even supposing that the new theories are fully accepted, the fact remains that the danger is not as great as we imagine, either for practical life or even for classical science, which is apparently menaced, and the mechanics of the old masters, apart from some modifications of detail, has still some centuries of existence before it.

We may here make a fundamental observation. Suppose that the only mass is electromagnetic mass, and that two masses must be distinguished, longitudinal and transversal. According to the admirable theories of Lorentz the values of these masses, worked out as a series, are composed of terms expressed by powers of the

$\frac{v}{c}$ , where  $v$  is the velocity of the moving particle and  $c$  the velocity of light, the first term being independent of  $v$ . So that—and this is important—if the velocity of motion is not comparable with the velocity of light, the fraction  $\frac{v}{c}$  would be so small that all its powers could be neglected, and the constant term, independent of  $v$ , would remain. Thus (Lorentz, "The Theory of Electrons," p. 39) the two masses  $m'$  and  $m''$ , for very small values of  $\beta$ , might be regarded as equal:—

$$m' = m'' = \frac{e^2}{6\pi R c^2}$$

and independent of  $v$ ; there is only one mass which is constant as far as velocity is concerned. Similar reasoning applies to most of the new theories.

Summarising we may say that classical mechanics is not the absolute truth, but the absolute truth is not to be found in classical science, nor in modern science, nor in modernism. Classical science is an approximation to absolute science—the first term of a series, so to speak; the following terms are new approximations which a newer science obtains, but which are very small in comparison with the first, as  $v$  is not comparable with  $c$ . Classical mechanics would be destroyed if the universe went mad, and the suns, the planets, the nebulae, the atoms, and everything which exists began to vibrate with velocities  $v$  comparable with  $c$ . And who knows if even then we could not fall back on relative velocities? For as long as the Cosmos remains moderate and moves with the relative velocities it possesses to-day, the old mechanics, the classical science of Newton, Galileo, Laplace, Lagrange runs no serious risk.

This does not diminish by one atom, since we are speaking of atoms, the scientific importance of new theories nor the great ingenuity and the profound ability revealed by their originators.

## VII.

But we have not finished with our negations; a large part, and that the most contentious, of the series still remains. We have said nothing of the negation which relates to the principle of the equality of action and reaction, nor of the principle of classical mechanics, which makes the action of forces depend only upon the geometrical relation holding good, without taking into consideration the actual velocities, or more generally the dynamical history of the system, a principle absolutely denied by criticism. Nor have we spoken of the problem of continuity and discontinuity, which is leading to the negation of continuity of energy, converting it into atoms. Planck discusses atoms of energy just as atoms of oxygen and hydrogen were formerly discussed. And thus we come to the negation of the legitimacy of the application of differential equations to mathematical physics, the extreme stage of negation, which has alarmed the powerful intellect and the vigorously critical spirit of H. Poincaré.

To bring our list to an end, we will mention one of the most obscure problems which is under discussion at the present moment, the problem of relativity and the negation of classical kinematics, for example, by the audacious suggestions of Einstein. We must defer the consideration of all these problems, but in conclusion we may say that, however serious they are, in our opinion the old mechanics will survive them all, provided that  $v$  is not comparable with  $c$ , as we have said before. The science of the nineteenth century will always remain the first and the most important term of a series of approximations, modern theories are the second term of it, and the most recent the third, while the science of the future will constitute the others. The important thing is that the series should be convergent.

### VIII.

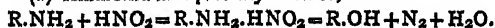
Thus, as Poincaré has said, mechanics, mathematical physics, classical science are passing through a critical period, but this crisis is not a death crisis, but a crisis of new life. The profound agitations of the period in which we are living are not the last convulsions of the death-agony, but the powerful movements of new birth.

#### NOTE ON THE ACTION OF NITROUS ACID ON THE AMINES.

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry,  
Government College, Rajshahi, Bengal, India.

In my paper entitled "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Interaction of the Hydrochlorides of the Bases and Alkali Nitrites—Explanation of the Action of Nitrous Acid on the Amines," published in the *CHEMICAL NEWS* (cviil., 53, 62), I elaborated my new theory of the action of nitrous acid on the amines which is summarised thus:—"The action of nitrous acid, nascent and free, on the primary, secondary, and tertiary amines, excepting purely aromatic amines, yields the corresponding amine nitrite as an intermediate compound, which, when heated, decomposes into alcohol and nitrogen in the case of primary amines, nitroso-compound in the case of secondary amines, and the free base together with the nitrate and nitric oxide in the case of tertiary amines according to the following equations:—

(a) Ammonia and primary amines,—



(b) Secondary amines,—



(c) Tertiary amines,—



At the present moment the decomposition products are regarded as the only products of the reaction. The reason is that, in studying the action of nitrous acid on the amines, mixtures of the amine hydrochlorides and alkali nitrites were simply heated, when of course the decomposition products only would be obtained. No one hitherto has subjected the mixtures to steam distillation in vacuum, when, as I have been able to show, the intermediate amine-nitrites distil over with the steam. It is to be noted that the amine-nitrites were discovered by Ray and Rakshit (*Trans. Chem. Soc.*, 1911 and 1912) by the double decomposition of amine hydrochlorides and silver nitrite at the ordinary temperature.

I have since then been able to confirm my theory by demonstrating the direct addition combination of free nitrous acid and free amines (*Trans. Chem. Soc.*, 1914, cv., 1270). Free nitrous acid is an unstable acid, and only momentarily stable at low temperatures in solutions. Using ice-cold solutions it was found that primary,

secondary, and tertiary amines do very nearly combine with free nitrous acid to form amine-nitrites, the operation being merely one of neutralisation of a weak acid and a strong base. Aromatic amines, such as aniline and its homologues, being very weak bases, do not combine with a weak acid like nitrous acid to form stable amine-nitrites. Aromatic amines, substituted in the side-chain and amines of the pyridine quinoline series being stronger bases, combine with nitrous acid to form more or less stable amine nitrites. This direct combination of free amines and free nitrous acid is the most important experimental evidence of my theory.

The whole question of the action of nitrous acid on the amines, therefore, will have to be looked into in an altogether different light. The action is one of simple neutralisation. Only those amines which are fairly strong would combine with nitrous acid to form amine-nitrites. It is not true, as is given in text-books on organic chemistry, that there is no action between tertiary alkyl amines and nitrous acid—as a matter of fact they being very strong bases, stronger than ammonia and primary amines, do very readily combine with nitrous acid. As has already been pointed out, the action of nitrous acid on the alkylamines has not hitherto been studied by the addition of free nitrous acid to free amines in the cold, but by simply heating mixtures of amine hydrochlorides and alkali nitrites, when of course the decomposition products of the amine-nitrites are obtained.

Purely aromatic amines being very weak bases do not combine additively with nitrous acid to form amine-nitrites. This inability of very weak bases to combine with nitrous acid sets up a new distinction between aliphatic and aromatic amines:—

#### Aliphatic Amines.

1. Primary amines form primary amine-nitrites which decompose, on heating, into alcohol and nitrogen.
2. Secondary amines form secondary amino-nitrites which decompose, on heating, into nitroso compounds.
3. Tertiary amines form tertiary amine-nitrites which, on heating, yield the free base, nitrate and nitric oxide.

#### Aromatic Amines.

1. Primary amines form diazo-compounds which decompose, on heating, into alcohol and nitrogen.
2. Secondary amines form nitroso-compounds directly.
3. Tertiary amines form corresponding nitroso-compounds.

The amine-nitrites have been here conveniently divided according to their properties into three classes—primary, secondary, and tertiary.

#### THE CHEMICAL INDUSTRIES OF GERMANY.\*

By Prof. PERCY F. FRANKLAND, F.R.S.

It is remarkable that the Royal House of Prussia has during many centuries been associated in one way or another with chemical enterprises of various kinds. Thus already the second ruler of the country, the Markgraf John (1608–1619) was actually surnamed "the Alchemist" in consequence of the zeal with which during many years he pursued his investigations on the transmutation of metals, whilst a number of his successors exhibited great interest in the same problem—the manufacture of gold—which has never failed to fascinate the needy princes—and what princes are not needy?—of all ages and all nations. The Great Elector (1640–1688), who did so much to advance the power of Prussia, was a patron of chemistry, which was just then beginning to emerge as an experimental science from the obscurantism of alchemy. He provided the

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when they have proved themselves to be a reality, a terrible negation, one might also say a sentence of death, falls on them. In the mind of physicists and chemists of the old school the atom was the simplest unit, indivisible, incorruptible, eternal. An atom of ponderable matter, an atom of oxygen, hydrogen, or nitrogen, passing through our laboratories came, according to unanimous opinion, from the depths of the past and of space in the form in which it reached us, and left our apparatus to pass to new abysses in the future, remaining always the same. The atom was eternal. The philosophers of the materialist school could call it a god: the god Atom. The invariability of mass, of which we have just been speaking, was explained by the invariability of the atom. And then comes a new negation, or a new series of negations—the atom is not invariable.

Moreover this is not a theory; the complexity of the atom, its decomposition, its disintegration, and its transformations can be seen, followed, and even measured. This is what radio-active substances and the whole theory of radio-activity tell us. It is true that originally radio-active substances were exceptions, but now we regard radio-activity as a general property of matter which is most marked in uranium, radium, and its congeners. Thus from the moment when the classical atom lost its unity and its prestige, and when each atom was regarded as an infinitely small but infinitely complex system, imagination leapt forward, and hypotheses concerning the constitution of these infinitesimal entities have multiplied.

We have Thomson's atom, with its central element of positive electricity in which the negative electrons are, so to speak, stamped in the form of rings; thus by the play of reciprocal attractions and repulsions equilibrium is established; sometimes it is lasting, and then the atom remains invariable, and sometimes it is destroyed, the number of rings and the number of electrons in each ring being invariable (*Phil. Mag.*, No. 39, March, 1904).

A new hypothesis converts the atom into a kind of planetary system, with its positive electron at the centre and its negative electrons not fixed, but revolving round it like planets. Without respect for the mystery of the atom we have increased its complexity, introducing into it a new system of magnetons.

Summarising, the extremely simple atom of the ancient atomic theories has become an electric complex in which all the hypotheses find an application and have distinguished protagonists. Without pretending to study them for the moment, and taking them altogether, we can deduce a powerful tendency to convert the traditional atom of ponderable matter into an electric system of extraordinary complexity: free atoms, rings, currents, magnetons, a whole electric world, without any explicit residue of ponderable matter.

Thus in this new theory ponderable matter disappears; everything is electricity in the universe—the negative electron, the positive electron, the electric current, and magnetism, which on Ampère's hypothesis is converted into a system of currents.

If the *modus vivendi* which we had established above, in order to preserve the invariability of ponderable matter, were what it pretended to be, it would be shattered and annihilated in the most disastrous way for the old matter of classical tradition. It is true that if ponderable matter does not exist as a special substance, essentially distinct from the electric fluid or electric atoms, there is no need to trouble about the invariability of mass of the old mechanics. Strictly speaking it is constant, since being non-existent it is equal to zero—a triumphant conclusion, the constancy of zero, the invariability of nothingness! But if ponderable mass does not exist, and if all mass is electromagnetic, all mass will be essentially variable and will depend upon the velocity. The negation which we have previously mentioned acquires an enormous force, and neither adaptations nor palliatives are any good: mass is essentially variable, and one of the pillars of classical mechanics has completely given way.

## VI.

Thus it appears at first sight, but there is no foundation for the fear. However ponderable matter is regarded, whether it is reduced to a collection of electric systems or not, even supposing that the new theories are fully accepted, the fact remains that the danger is not as great as we imagine, either for practical life or even for classical science, which is apparently menaced, and the mechanics of the old masters, apart from some modifications of detail, has still some centuries of existence before it.

We may here make a fundamental observation. Suppose that the only mass is electromagnetic mass, and that two masses must be distinguished, longitudinal and transversal. According to the admirable theories of Lorentz the values of these masses, worked out as a series, are composed of terms expressed by powers of  $\frac{v}{c}$ , where  $v$  is the velocity of the moving particle and  $c$  the velocity of light, the first term being independent of  $v$ . So that—and this is important—if the velocity of motion is not comparable with the velocity of light, the fraction  $\frac{v}{c}$  would be so small that all its powers could be neglected, and the constant term, independent of  $v$ , would remain. Thus (Lorentz, "The Theory of Electrons," p. 39) the two masses  $m'$  and  $m''$ , for very small values of  $\beta$ , might be regarded as equal:—

$$m' = m'' = \frac{e^2}{6\pi R c^2}$$

and independent of  $v$ ; there is only one mass which is constant as far as velocity is concerned. Similar reasoning applies to most of the new theories.

Summarising we may say that classical mechanics is not the absolute truth, but the absolute truth is not to be found in classical science, nor in modern science, nor in modernism. Classical science is an approximation to absolute science—the first term of a series, so to speak; the following terms are new approximations which a newer science obtains, but which are very small in comparison with the first, as  $v$  is not comparable with  $c$ . Classical mechanics would be destroyed if the universe went mad, and the suns, the planets, the nebulae, the atoms, and everything which exists began to vibrate with velocities  $v$  comparable with  $c$ . And who knows if even then we could not fall back on relative velocities? For as long as the Cosmos remains moderate and moves with the relative velocities it possesses to-day, the old mechanics, the classical science of Newton, Galileo, Laplace, Lagrange runs no serious risk.

This does not diminish by one atom, since we are speaking of atoms, the scientific importance of new theories nor the great ingenuity and the profound ability revealed by their originators.

## VII.

But we have not finished with our negations; a large part, and that the most contentious, of the series still remains. We have said nothing of the negation which relates to the principle of the equality of action and reaction, nor of the principle of classical mechanics, which makes the action of forces depend only upon the geometrical relation holding good, without taking into consideration the actual velocities, or more generally the dynamical history of the system, a principle absolutely denied by criticism. Nor have we spoken of the problem of continuity and discontinuity, which is leading to the negation of continuity of energy, converting it into atoms. Planck discusses atoms of energy just as atoms of oxygen and hydrogen were formerly discussed. And thus we come to the negation of the legitimacy of the application of differential equations to mathematical physics, the extreme stage of negation, which has alarmed the powerful intellect and the vigorously critical spirit of H. Poincaré.



To bring our list to an end, we will mention one of the most obscure problems which is under discussion at the present moment, the problem of relativity and the negation of classical kinematics, for example, by the audacious suggestions of Einstein. We must defer the consideration of all these problems, but in conclusion we may say that, however serious they are, in our opinion the old mechanics will survive them all, provided that  $v$  is not comparable with  $c$ , as we have said before. The science of the nineteenth century will always remain the first and the most important term of a series of approximations, modern theories are the second term of it, and the most recent the third, while the science of the future will constitute the others. The important thing is that the series should be convergent.

### VIII.

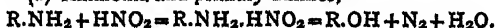
Thus, as Poincaré has said, mechanics, mathematical physics, classical science are passing through a critical period, but this crisis is not a death crisis, but a crisis of new life. The profound agitations of the period in which we are living are not the last convulsions of the death-agony, but the powerful movements of new birth.

### NOTE ON THE ACTION OF NITROUS ACID ON THE AMINES.

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry,  
Government College, Rajshahi, Bengal, India.

IN my paper entitled "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Interaction of the Hydrochlorides of the Bases and Alkali Nitrites—Explanation of the Action of Nitrous Acid on the Amines," published in the CHEMICAL NEWS (cviii., 53, 62), I elaborated my new theory of the action of nitrous acid on the amines which is summarised thus:—"The action of nitrous acid, nascent and free, on the primary, secondary, and tertiary amines, excepting purely aromatic amines, yields the corresponding amine nitrite as an intermediate compound, which, when heated, decomposes into alcohol and nitrogen in the case of primary amines, nitroso-compound in the case of secondary amines, and the free base together with the nitrate and nitric oxide in the case of tertiary amines according to the following equations:—

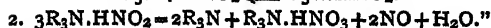
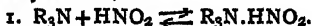
(a) Ammonia and primary amines,—



(b) Secondary amines,—



(c) Tertiary amines,—



At the present moment the decomposition products are regarded as the only products of the reaction. The reason is that, in studying the action of nitrous acid on the amines, mixtures of the amine hydrochlorides and alkali nitrites were simply heated, when of course the decomposition products only would be obtained. No one hitherto has subjected the mixtures to steam distillation in vacuum, when, as I have been able to show, the intermediate amine-nitrites distil over with the steam. It is to be noted that the amine-nitrites were discovered by Ray and Rakshit (*Trans. Chem. Soc.*, 1911 and 1912) by the double decomposition of amine hydrochlorides and silver nitrite at the ordinary temperature.

I have since then been able to confirm my theory by demonstrating the direct addition combination of free nitrous acid and free amines (*Trans. Chem. Soc.*, 1914, cv., 1270). Free nitrous acid is an unstable acid, and only momentarily stable at low temperatures in solutions. Using ice-cold solutions it was found that primary,

secondary, and tertiary amines do very nearly combine with free nitrous acid to form amine-nitrites, the operation being merely one of neutralisation of a weak acid and a strong base. Aromatic amines, such as aniline and its homologues, being very weak bases, do not combine with a weak acid like nitrous acid to form stable amine-nitrites. Aromatic amines, substituted in the side-chain and amines of the pyridine quinoline series being stronger bases, combine with nitrous acid to form more or less stable amine nitrites. This direct combination of free amines and free nitrous acid is the most important experimental evidence of my theory.

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celebrated Kunkel with a laboratory and glass furnaces on an island in his park at Potsdam, and it was there that in 1678 Kunkel made the discovery of ruby glass, produced by means of traces of gold, and which is still an unsurpassed method of colouring glass for ornamental purposes. Kunkel also re-discovered phosphorus, which had previously, in 1669, been obtained by the alchemist Brand, of Hamburg, who had quite accidentally produced it in the course of his attempts to extract the Philosopher's Stone out of urine. But whilst the discovery of yellow phosphorus is thus of German origin, its production on an industrial scale was, until twenty years ago, only carried on in England and France. In 1892 the manufacture of phosphorus by electro-thermic means was introduced into Germany by the Chem. Fab. Griesheim-Elektron at Frankfurt. (The author has much pleasure in acknowledging the assistance he has received from the valuable compilation by Prof. Lepsius of Berlin, "Deutschlands Chem. Industrie," 1888-1913, and from that by Dr. Dniseberg, of Elberfeld, "Wissenschaft und Technik," 1911.) Red phosphorus was discovered by Schrotter, an Austrian chemist, in 1848, and was adopted for safety-matches by the German Bottger in the same year. His invention was first taken up in Sweden, and was not adopted until ten years later in Germany. The match industry has assumed its largest dimensions in Germany. Thus the German annual production in 1912 was £4,600,000 (Molinari, "General and Industrial Inorganic Chemistry," 1912). The value of all matches (British and foreign) consumed in Great Britain in 1910 is estimated at £1,293,750 - about nine matches per day per head. Messrs. Bryant and May's (by far the largest English concern) turned out 1152 million boxes in 1907. This represents about half the British output. In 1907 the total value of British production was £775,000, of which £76,000 worth was exported (Clayton). The British export of matches is diminishing. It is worthy of note that Japan in 1901 exported matches to the value of £1,200,000.

**Porcelain.**—Another great German industry owes its origin to alchemistic studies made by Böttcher in the reign following that of the Great Elector, namely, that of Frederick III. (1688-1713), first King of Prussia. Having succeeded in making gold before witnesses, Böttcher was seized by order of the Elector of Saxony and was "interned" at Dresden, where, although he did not succeed in making the much-desired gold, he founded, along with the physicist Tschirnhaus, the celebrated Dresden porcelain industry.

The astute Frederick the Great (1740-1786) was anxious to manufacture the Dresden ware at Berlin and to this end commissioned his court apothecary, Johann Heinrich Pott, to institute investigations. These attempts were, however, all unsuccessful.

The Great Frederick placed much faith in secret agents, and it was by means of spies that he succeeded in discovering the secrets of the Dresden porcelain manufacture, for at his instigation an enterprising merchant, bearing the name of Gotzkowski, with the assistance of a Saxon workman, brought the secrets of the Dresden process to Berlin and established a porcelain factory in the Leipzigerstrasse, which still remains the warehouse for the Berlin porcelain goods. But Frederick later stopped the pecuniary assistance with which the factory had been subsidised, and Gotzkowski was forced to sell the concern to Frederick for a sum of about £30,000, and so was established the celebrated Berlin Royal Porcelain Factory, amongst the products of which are the well-known crucibles and evaporating basins. The flourishing state of the German porcelain and pottery manufacture is attested by the fact that during the past twenty-five years the number of works has increased from 228 to 359, and the number of workpeople employed from 37,000 to 66,000. In 1912 the German exports of china, earthen and stoneware were valued at upwards of 3½ millions sterling.

**Glass.**—Even still more important is Germany's glass

manufacture, for which she has long been pre-eminent. The annual export in recent years has been over seven million pounds.

**Cyanide Industry.**—In the early eighteenth century an accidental discovery was made by Diesbach, a Berlin colour-maker, which has proved of great industrial importance. Diesbach was preparing what is known as Florentine lake, a red pigment obtained by precipitating a solution containing cochineal extract and an iron salt with caustic potash. It so happened, however, that the potash used by Diesbach had been in contact with bone-oil, containing some cyanide, and the result was that, instead of the result he anticipated, a magnificent blue colouring matter was obtained. This substance, which is still known as Berlin or Prussian blue, was the first cyanogen compound to be discovered.

The cyanogen compounds have played a most conspicuous part in the development of organic chemistry, and every source of cyanogen has been exploited for obtaining them. In recent years the demand has increased enormously owing to the employment of sodium and potassium cyanides in the extraction of gold. To meet this demand a number of synthetical methods for their preparation have been super-added.

Germany's annual production of cyanides is estimated at 10,000 tons, of value £650,000, or about half of the world's production.

**Beet-sugar Industry.**—Another industry also had its beginnings in the 18th century during the reign of the Great Frederick, and was the outcome of the laborious researches of Marggraf (born in Berlin in 1700, and a pupil of Stahl) on the occurrence of sugar in the vegetable kingdom. Of the numerous plants investigated from this point of view he found that the beetroot (*Beta vulgaris*) contained the largest proportion of saccharine material, and that the sweet-tasting substance was identical with that present in the tropical sugar cane (*Saccharum officinarum*).

It was not, however, until some fifty years later that the observation of Marggraf led to the first beet-sugar factory in the hands of Franz Karl Achard, who was subsidised in this venture by the Prussian King, Frederick William III. (reign 1797-1840), who was also the founder of the University of Berlin.

(NOTE.—There was no university in Berlin until 1809, but the following figures will show how Prussia has made up for lost time in this respect. In 1913-14, there were 7613 male and 770 female matriculated students, and 4113 male and 89 female non-matriculated students. The annual income was £246,310, of which £204,650 came from the State, £40,900 from fees, &c., and £760 from other sources. The annual expenditure was £246,310, of which the teaching staff accounted for £104,790; departmental expenses, £100,140; building expenses, £10,610; reserve, £6680; administration, bursaries, &c., £24,090. "Minerva," 1914).

The beet-sugar industry had to contend with strenuous competition on the part of the cane-sugar manufacturers, who were chiefly English and who are said to have endeavoured to corrupt Achard by heavy bribes. The industry was, however, greatly promoted when, in 1806, Napoleon issued his famous edict closing the European ports to British goods. The vast extent of this industry at the present time can be gathered from the following figures:—

Total sugar crop for 1912-13: Cane-sugar, 9,211,755 tons; beet-sugar, European (one-third German), 8,310,000 tons; beet-sugar, U.S.A., 624,064 tons; total, 18,145,819 tons.

The sugar industry should give us food for serious reflection when we consider the following facts:—United Kingdom spends annually £23,000,000 on 1,700,000 tons imported sugar. Germany produces £36,000,000 worth of beet-sugar on 1,300,000 acres; France produces £13,000,000 on 570,000 acres; all continental countries together produce £116,000,000 on 6,000,000 acres (C. W. Fielding, *Morning Post*, Jan. 23, 1913). In the

	Production in Tons, 1910. (a)					
	Germany.	England	France.	United States.	Europe.	World.
Sulphuric acid ( $H_2SO_4$ ) . . . .	1,250,000	1,000,000	500,000	1,200,000	3,700,000	5,000,000
(of this by contact process) . .	400,000			250,000		
Soda . . . . .	400,000	700,000	200,000	250,000		2,000,000
(of this Le Blanc soda) . . . .	30,000	120,000				150,000
Salt-petre consumption . . . .	786,000	93,000	337,000	523,000	1,740,000	2,360,000
(of this for nitric acid) . . . .	150,000			50,000		
Hydrochloric acid (30 per cent) .	450,000	(b)				
Bleaching powder . . . . .	100,000					300,000
(of this electrolytic) . . . . .	70,000					150,000

(a) Duisberg, "Wissenschaft und Technik," 1911.

(b) Already in 1895 the estimated production of hydrochloric acid in England was 1 million tons, and for the whole of Europe 2 million tons (Molinari).

United Kingdom there is only one small experimental beet sugar factory in existence. The beet-sugar industry is of particular interest in connection with the present European crisis, inasmuch as it is a most notable example of an industry which largely owed its successful inception to a state of war which disturbed the previously established order of things in the matter of sugar supply.

In this country agriculture is well known to be productive of a conservative frame of mind, but that it is not so in Germany is well illustrated by the extraordinary progress which has been made in the cultivation of the sugar-beet under the guidance of systematic scientific research. Thus in 1840, 100 kilos. of beet gave 5.9 kilos. sugar; in 1850, 7.3; in 1870, 8.4; in 1890, 12.5; and in 1910, 15.8 kilos. In 1871 the mean production of beet per hectare (hectare = 2.5 acre) was 246 quintals (1 quintal = 100 kilograms.), and in 1910, 300 quintals. In 1867 the consumption of coal for 100 kilos. of beet was 35 kilos.; in 1877, 24; in 1890, 10; and in 1900, 7 kilos. Further economy in coal has been effected by means of the Kestner concentrator (Molinari, "General and Industrial Org. Chem.," 1913).

**Sulphuric Acid, Soda, and Bleaching Powder Industries.**—Sulphuric acid was discovered by the German alchemist Basil Valentine in the 15th century. The production of this fundamental acid, however, on any considerable scale took its origin in Birmingham, where Dr. Roebuck in 1746 introduced the classical leaden chamber process. At the beginning of the 19th century it became an industry of great importance, more especially in England, because of this acid being required for the manufacture of carbonate of soda by the Le Blanc process.

The manufacture of Le Blanc soda was taken up in England in 1814, especially in connection with soap-making, and it was in England that this manufacture assumed the largest proportions. The enormous advances made in this manufacture during the past century may be gathered from the fact that the price of carbonate of soda in 1818 was about £42 per ton, whilst to day it is only about one-tenth of that amount. One of the determining factors which made England the principal home of soda manufacture was the great development of our cotton industry during the 19th century.

During a large part of the last century England manufactured Le Blanc soda, sulphuric acid, and bleaching powder (discovered by Tennant in 1799) for most of the world. But during the latter half of the century the rival ammonia soda process made its appearance. The original discovery of the reaction on which it depends—it was first patented in England by Dyer and Hemming in 1838—is ascribed to several different persons, but the process was first made an industrial success in Belgium by M. Ernest Solvay. The Couillet Works were founded with a capital of about £6000 in 1863; the numerous affiliated works are now to be found in Belgium, England (Brunner, Mond, and Co.), Germany, France, Italy, Spain, Austria-Hungary, Russia, and North America. They employ 35,000 persons. During the fifty years the price of soda has been reduced from £16 to £4 a ton. The displacement of Le Blanc soda by ammonia soda involves the

introduction of new methods of chlorine manufacture. After numerous abortive attempts in various directions, the successful production of electrolytic chlorine has been achieved, and about half of the bleaching powder in the world is now made by this means.

Electrolytic chlorine is now often converted into liquid chlorine (6d. a kilo.), of which large quantities are used at Stassfurt for the annual preparation of 500,000 kilograms. of bromine, and the Badische Anilin und Soda Fabrik used in 1900 more than 1 million kilos. for the preparation of chloroacetic acid employed in the manufacture of synthetic indigo.

In the manufacture of sulphuric acid, again, the old-established English or leaden chamber process has not been allowed to remain unchallenged, for since the beginning of the present century it has had to meet the competition of the so-called contact process. This is based on a long known reaction, which, however, remained almost unutilised until the meticulous industry of German chemists and the courageous enterprise of German manufacturers developed it into a commercially successful process, which was elaborated in the works of the Badische Aniline und Soda Fabrik at Ludwigshafen. (This reaction had for many years been used by Messel in England, but only for manufacture of  $SO_3$ ).

The ammonia-soda and the contact sulphuric acid processes, although carried out in this country, have been largely instrumental in making other countries, more especially Germany and the United States, independent of the English production of these all-important chemicals. (The Clayton Aniline Co. and Nobel's Explosive Works have contact sulphuric acid plant).

In 1882 the world's consumption of soda was 700,000 tons (160,000 am. soda), and in 1902 1,760,000 tons (250,000 Le Blanc). In England in 1876 £7,000,000 was invested in the industry, which gave employment to 22,000 workpeople. In 1880 the British output was 430,000 tons and in 1896 800,000 tons. North America in 1886 produced 1100 tons, and in 1898 300,000 tons, and Germany in 1878 made 42,000 tons, in 1901 300,000 tons, and in 1910 400,000 tons (Molinari). The first soda works in Germany was only erected in 1843 by Hermann at Schönebeck, near Magdeburg, and the first leaden chamber by Kunheim in 1844 on the Tempelhof Plain, near Berlin.

(To be continued)

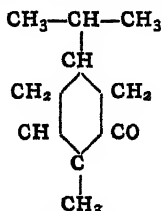
**Royal Society of Arts.**—The Albert Medal of the Royal Society of Arts for the current year has been awarded by the Council, with the approval of the President, H.R.H. the Duke of Connaught and Strathearn, K.G., to Prof. Sir Joseph John Thomson, O.M., D.Sc., LL.D., F.R.S., for his researches in physics and chemistry, and their application to the advancement of arts, manufactures, and commerce. The Albert Medal was founded in 1863 to commemorate the Prince Consort's Presidency of the Society, and is awarded for "distinguished conduct in promoting arts, manufactures, and commerce."

## CAMPHOR: NATURAL AND SYNTHETIC.\*

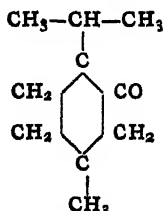
By PERCY A. HOUSEMAN, Ph.D., F.I.C.

(Concluded from p. 248.)

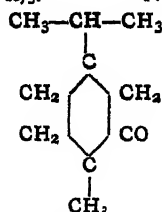
FORMULA IV. was put forward by Kannonikow in 1883 and V. by Bredt in 1884. That Bredt was correct and Kannonikow incorrect in the position assigned to the carbonyl group is proved by the conversion of camphor to carvacrol, considered above.



III. Kekulé, 1873.

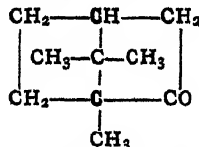


IV. Kannonikow, 1883.

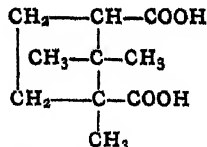


V. Bredt, 1884.

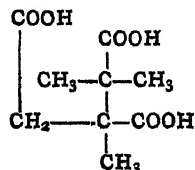
Bredt later modified his formula to that shown by VI. The oxidation of camphor to camphoric acid is then formulated as follows:—



VI. Camphor (Bredt, 1893).



VII. Camphoric acid.

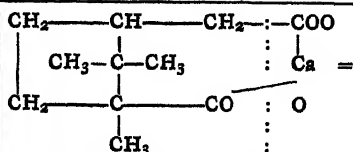


VIII. Camphoric acid.

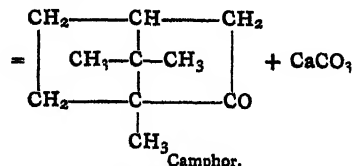
Camphoric acid has been synthesised, and is of known constitution ( $\alpha$ - $\alpha$ - $\beta$ -trimethyl tricarballic acid). Lastly, two other points may be mentioned in connection with this complicated question of the structure of camphor.

The first is the partial synthesis of camphor by the distillation of the calcium salt of homocamphoric acid (IX.) (Bredt and Rosenberg. *Ann. der Chem.*, 289). This reaction is shown at top of next column.

The second point is the evidence derived from stereochemical considerations. From Formula VI. it will be seen that camphor contains two asymmetric carbon atoms (printed in heavy type). To these asymmetric atoms camphor owes its optical activity. If now the carbonyl CO group be reduced to  $\text{CH}_2$ , the asymmetry of both carbon atoms is destroyed, and the resulting compound must be inactive. This is entirely supported by the experimental results. Bredt's formula for camphor is the only one to interpret satisfactorily all the reactions discussed above, and his formula is now generally accepted.

\* *Chemical Engineer*, xxi., No. 2.

IX. Calcium homocamphorate.



## Synthetic Camphor.

The raw material for the synthesis of camphor is turpentine, the resinous liquid exuding from various *Coniferae*. American turpentine is mostly obtained from *Pinus palustris*, the French variety from *Pinus maritima*, and the Russian from *Pinus sylvestris*. Russian turpentine is not suitable for the manufacture of camphor, on account of its low content of pinene.

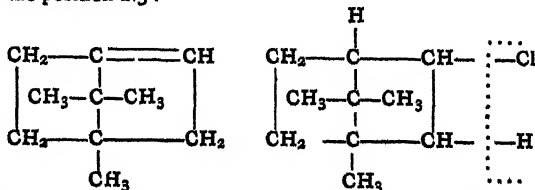
The turpentine is very carefully fractionally distilled in order to obtain anhydrous pinene,  $\text{C}_{10}\text{H}_{16}$ , which boils at about  $155^\circ$  to  $160^\circ \text{C}$ ., and which should constitute 90 per cent of a good sample of oil of turpentine.

Starting out from pinene, there are a great number of variations in the processes for the preparation of camphor. Hundreds of patents have been taken out (*cf.*, O. Kausch, *Kunststoffe*, iv., 1-4, 24-5; F. Rochussen, *Chem. Zeit.*, 1909, xxxiii., 704). Some of the typical processes will be mentioned here.

In many of the processes the pinene is thoroughly cooled, and is then saturated with dry hydrochloric acid gas. A white crystalline mass of pinene hydrochloride is thrown out. Pinene hydrochloride is sometimes called "Artificial camphor"—an unfortunate name, for it is still far removed from the true synthetic camphor, and is not suited to the purposes for which true camphor is used.

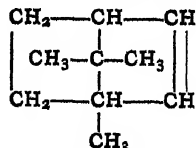
The next step is to split off hydrochloric acid from the pinene hydrochloride, in order to obtain the hydrocarbon camphene,  $\text{C}_{10}\text{H}_{16}$ , which is isomeric with the pinene from which the process started.

The following formulae indicate the first two steps—the addition of hydrochloric acid to pinene in the position 1,2, and its removal from another part of the molecule, viz., the position 2,3:—



X. Pinene.

XI. Pinene hydrochloride.



XII. Camphene.

The conversion of pinene hydrochloride to camphene may be accomplished in a great variety of ways, among which may be mentioned:—

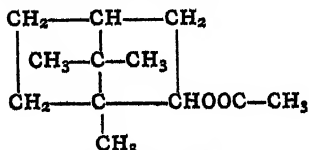
1. Heating with ammonia or with organic bases, such as methylamine, pyridine, quinoline, piperidine, or piperazine.

2. Heating with caustic soda and a salt of a higher fatty acid, such as stearates of sodium, lead, or copper,
3. Heating with phenolates or naphtholates of sodium, potassium, calcium, magnesium, &c.
4. Heating with glacial acetic acid and anhydrous acetates of lead, zinc, or alkaline earth metals.
5. Treatment with magnesium as used in the Grignard reaction.

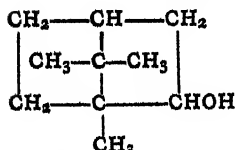
It is worthy of note that camphene is the only solid terpene hydrocarbon. It is a white solid melting at 50° C.

The next stage in the process is the conversion of camphene to bornyl acetate. (The term bornyl acetate and borneol are used for simplicity. In reality iso-bornyl acetate and iso-borneol are produced. The nature of the isomerism is not clearly understood). This is accomplished, as Bertram and Walbaum showed (*Journ. Prakt. Chem.*, xlix., 1), by treating the solution of the camphene in glacial acetic acid with about 5 per cent of sulphuric acid at a slightly elevated temperature. Acetic acid is added on, in accordance with the formula below. Bornyl acetate is an oil boiling with some decomposition at about 225° C. It is readily volatile in steam.

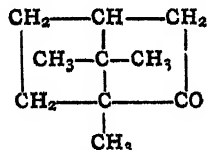
The final steps in the camphor synthesis consists in the saponification of the bornyl acetate to borneol, and the oxidation of the borneol to camphor.



XIII. Bornyl acetate.



XIV Borneol



XV. Camphor

The saponification is accomplished with alcoholic caustic soda, yielding sodium acetate as a by-product. The borneol so obtained is, with the exception of its optical inactivity, identical with the Borneo camphor occurring in nature.

The oxidation of borneol to camphor can be accomplished by a great variety of oxidising agents—air, ozone, chlorine, nitric acid, potassium permanganate, potassium bichromate, and sulphuric acid, and finely-divided metals such as nickel and cobalt (Schering, German patents 271147 and 271157; also patent of Port Chester Chemical Company, New York, 1911). When potassium bichromate and sulphuric acid are used, chrome alum is obtained as a by-product.

The type of process outlined above thus involves six distinct stages before the final product is obtained:—

Turpentine → pinene → pinene hydrochloride → camphene → bornyl acetate → borneol → camphor.

According to a German process, the anhydrous rectified oil of turpentine is heated directly with anhydrous oxalic acid. Some camphor is formed, and the oxalic and formic esters of pinene, which are also present, are saponified and oxidised. Salicylic acid may also be employed instead of oxalic acid.

The crude camphor obtained by any of these methods is refined by steam distillation or sublimation, in the same manner as the crude natural camphor is purified.

#### Properties of Synthetic Camphor.

Synthetic camphor is identical with the natural article in all its chemical and physical properties, with the exception (in common with other synthetic organic compounds)

that it is optically inactive. The question of the differences of physiological action of the dextro, lævo, and synthetic modifications appears not to be settled (Langgaard and Maass, *Therapeut. Monatsh.*, 1907, xx., 573; Bruni, *Gazz. Chem. Ital.*, 1908, [2], xxxviii., 1; Hamalainen, *Skau. Arch. fur Physiol.*, 1908, xxi., 64). The differences seem to be of degree and not of kind (see, e.g., W. E. Grove, *Journ. Pharm.*, i., 445). Johnstone (*Pharm. Journ.*, lxxxiii., 534) makes a plea for the recognition of synthetic camphor in the British pharmacopœia, on the ground of its therapeutic equivalence to natural camphor.

As regards the chemical purity of synthetic camphor, celluloid manufacturers state that it must be quite free from chlorine for use in the preparation of celluloid.

#### History and Future of Camphor.

The short history of synthetic camphor since it was first made about ten years ago has been a very troubled one, and the future of the industry still seems to be a matter of great uncertainty. This chequered career has been caused largely by a great fluctuation in the price of natural camphor. Forty years ago the price of Japanese camphor was about 8 cents per pound. The Japanese Government assumed a monopoly of camphor in 1899, after the Sino-Japanese War. In 1903 the price was about 30 cents per pound. At the time of the Russo-Japanese War, in 1905, the price of camphor rose to over a dollar per pound, and in 1906 and 1907 it was about 60 cents per pound. While camphor was at its highest price chemists succeeded in working out the synthetic processes outlined above, and the manufacture was commenced in Germany, France, and England. In 1909 the Japanese, with large stores on hand, reduced the price of Japanese camphor to about 30 cents per pound, a price at which it was impossible to manufacture the synthetic article. The French and English companies were unable to overcome financial difficulties, and it is believed that in 1910 only one factory was still making synthetic camphor—the Chemische Fabrik a. A. vorm. E. Schering. The price of camphor at the end of 1910 was about 35 cents per pound, and the profits from the Formosan monopoly for the fiscal year ending March 31, 1910, amounted to no less than 1,982,966 dols. with a total production of 4,000,000 kgrms. (*"Chem. Abst."*, 1910, 3120). During the last four years the price of camphor has not varied greatly, but the outbreak of the present war has resulted in another rapid advance in price to about double the normal value.

Synthetic camphor is now being manufactured in Germany by the Rheinische Kampfer Fabrik in Dusseldorf. How long this company will be able to continue in operation is a matter of conjecture.

When much is being said of the opportunity of American chemical manufacturers to produce materials hitherto imported from Germany, it is gratifying to be able to record that a start is to be made on the manufacture of synthetic camphor in Philadelphia, early in 1915, by the American Camphor Corporation.

As to the future of synthetic camphor, it would be rash to prophesy.

The Japanese Government is now thoroughly alive to the importance of the conservation of camphor trees. Extensive re-planting has been commenced, but many years will elapse before these trees will yield camphor. All of the trees in readily accessible locations have been cut down, and, though immense camphor forests still exist, they are in mountainous districts of the interior, inhabited by savage tribes.

Synthetic camphor has had other enemies besides its Oriental rival. The price and supply of turpentine have been subject to considerable variation. The American manufacturer should, however, have less reason than his European competitors to fear a shortage of turpentine.

Then, again, a substance may be found capable of replacing camphor in celluloid, or a substitute may be found for celluloid itself (e.g., German Patent 219918, 1908, Chem. Fabrik Griesheim-Elektron, which covers



the use of dioxidyphenylsulphone). A great many experiments have already been made in this direction, largely on account of the inflammable nature of celluloid, and the work of Cross and Bevan, Knoll and Knoevenagel, and others, on the non-inflammable esters of cellulose, may supply a satisfactory substitute for celluloid in the near future.

All of these questions are matters of speculation, which time will answer. In any case, synthetic camphor, whatever its commercial future may be, stands as a splendid example of achievement in the field of chemical synthesis.

## THE PRODUCTION AND FERTILISER VALUE OF CITRIC-SOLUBLE PHOSPHORIC ACID AND POTASH.\*

By WM. H. WAGGAMAN,  
Scientist in Investigation of Fertiliser Resources.

### Introduction.

THE extraction of potash from silicate rocks or the rendering of this alkali soluble in water has been, and probably will continue to be for a long time, the object of numerous investigations.

Ross has investigated many of these processes, and discussed several in some detail (*Journ. of Ind. and Eng. Chem.*, 1913, v., No. 9, 725). For convenience he divides them into three classes, as follows:—(1) Processes which yield potash as the only product of value; (2) processes which yield potash and some other saleable material as a by-product; (3) processes in which two or more operations are combined in one, yielding a fertiliser containing two or more of the constituents—potash, phosphoric acid, and nitrogen. He describes two methods for obtaining potash from felspar by treating mixtures of that mineral and lime, collecting the potash thus liberated, and using the residue for the manufacture of cement. The potash obtained by these processes, however, is in the form of oxide or hydroxide, and is therefore more valuable for other purposes than for the manufacture of fertilisers. Ross also tried heating together felspar and lime with the addition of phosphate rock, but found that the latter substance did not enter into the reaction, there being no increase in the quantity of potash thus obtained over that produced by the ignition of felspar and lime alone.

The production in a single operation of available phosphoric acid and potash from insoluble minerals, however, presents possibilities which are particularly attractive, and several processes have been devised to accomplish this end. It is the purpose of this paper first to discuss these existing methods, and then to describe a process recently devised in this laboratory for rendering the phosphoric acid and potash in a mixture of phosphatic limestone and felspar "citric soluble."

### Earlier Methods.

There are four recorded processes for making a phosphoric acid-potash fertiliser from phosphate rock and felspar. (Since transmitting this manuscript several other processes have been devised. The author regrets that it is impracticable to consider these methods in the present paper). In chronological order they are as follows:—

A method devised by Charles Bickell in 1856 (U.S. Patent No. 16111, 1856), which consists in heating in a reverberatory furnace to a light redness for two hours an intimate mixture of one part felspar, 0.5 part phosphate of lime, and three or four parts of air-slaked lime. Bickell claims that both phosphoric acid and potash in available forms are obtained by this treatment.

This experiment was repeated in this laboratory, using felspar, Tennessee phosphatic limestone, and calcium carbonate in the following proportions:—

	Per cent.
Felspar (13.7 per cent $K_2O$ ) .. .. .	22.2
Phosphatic limestone (23 per cent $P_2O_5$ ) ..	11.1
Calcium carbonate .. .. .	66.7

Assuming that the carbon dioxide present in the calcium carbonate and phosphatic limestone was the only substance volatilised during the process, the product should have contained after ignition 4.38 per cent potash ( $K_2O$ ) and 3.4 per cent phosphoric acid ( $P_2O_5$ ). Analysis of the residue, however, gave the following results:—

$K_2O$ :—	Per cent.
Total .. .. .	1.94
Water soluble .. .. .	0.18
$P_2O_5$ :—	
Total .. .. .	3.62
Citric soluble .. .. .	1.40

These results show that over 44 per cent of the potash present in the mixture was volatilised upon ignition, and of that which remained in the residue only 9 per cent was water soluble. While none of the phosphoric acid was volatilised, less than 39 per cent of the total amount present was soluble in a 2 per cent solution of citric acid (the method usually employed for determining the availability of phosphoric acid in basic slag).

The second process for the manufacture of a phosphate-potash fertiliser from felspar and phosphate rock was devised by Frederick Klett in 1865 (U.S. Patent No. 49891, 1865). It consists of heating to redness for five hours an intimate mixture of one part felspar, two parts carbonate of lime, one part phosphate rock, and adding for each part of  $K_2O$  in the felspar two parts of calcium fluoride. It is claimed that a soluble silicate of lime and potassium phosphate are thus obtained. In view of the fact that the percentage of potash in the mixture is relatively small and that the time of heating is very long, it is hardly likely that the value of the product would cover the cost of manufacture. Moreover, the claim that phosphate of potash is formed in the operation is apparently not justifiable. It was thought advisable, however, to test this process also. A mixture of the following composition was made up and ignited in a muffle furnace for five hours at red heat:—

	Per cent
Felspar (13 per cent $K_2O$ ) .. .. .	24.21
Phosphate rock (32.8 per cent $P_2O_5$ ) ..	24.21
Calcium carbonate .. .. .	48.42
Calcium fluoride .. .. .	3.15

The slightly sintered product of this mixture was finely ground and analysed both for potash and phosphoric acid. If carbon dioxide were the only volatile substance formed by heating the above mixture the final product should have contained 4 per cent of  $K_2O$  and 10.09 per cent of  $P_2O_5$ . Actual analysis of the material, however, gave the following results:—

$K_2O$ :—	Per cent.
Total .. .. .	0.60
$P_2O_5$ :—	
Total .. .. .	10.51
Citric soluble .. .. .	4.15

Here again, as in Bickell's process, the potash nearly all volatilised, while less than one half of the phosphoric acid present in the residue is citric soluble.

The third process for rendering the phosphoric acid and potash of rocks available for fertiliser purposes is that of Coates (U.S. Patent No. 947795, 1910), which consists in adding to the sterilised rock mixture certain micro-organisms that effect the breaking down of the rock minerals. It is understood that the material thus prepared is being tried out experimentally by actual field tests, the results not yet having been reported.

\* Bulletin 148, U.S. Department of Agriculture, Bureau of Soils.

In 1912 Haff (U.S. Patent No. 108186, 1912) devised a process for making potassium sulphate from a mixture of felspar and phosphate rock. The method is based on the fact that at high temperatures and in the presence of silica and a non-volatile base both potash and phosphoric acid are volatilised. Haff claims that 95 per cent of the potash and phosphoric acid of natural rocks can be driven off at a temperature of 2000° C., and collected by passing the fumes through scrubbing towers. While this method has not been tried out in this laboratory, the cost of maintaining the high temperature necessary for the decomposition of the minerals and the expense of collecting and recovering the potash and phosphoric acid thus volatilised make it very doubtful if this process is commercially practicable.

#### *The Fusion of Felspar and Phosphate Rock.*

The solubility of phosphates in certain organic solutions has for a long time been regarded as a test of their agricultural availability. The nature and strength of the organic solvent used differs in various countries, and since each process is based on an arbitrary standard, it can only give corresponding results when conditions are the same. But, in spite of the fact that none of these methods is founded upon a strictly scientific basis, it is generally thought that phosphates soluble in such solutions are under soil conditions more active than those which do not dissolve in the same mediums.

The beneficial effect of the phosphoric acid in finely ground steamed bone is unquestioned, and although little of it is water soluble, a neutral solution of ammonium citrate will dissolve from 12 to 31 per cent of the acid, depending on the temperature of the solution and the time of contact (H. A. Huston, 32nd Annual Report Indiana State Board of Agriculture, 1883, 230; H. W. Wiley, "Principles and Practice of Agricultural Analysis," ii., 47; H. J. Wheeler, "Manures and Fertilisers," 1913, 172). It is also an indisputable fact that excellent results have been obtained by the use of basic slag as a fertiliser, and it is claimed that these results are commensurate with the amount of citric soluble phosphoric acid present in the material.

It has therefore become customary to regard citrate or citric soluble phosphoric acid as having a commercial value nearly equal to that of water soluble phosphate. (A report of a conference of the experiment stations of New York, New Jersey, and New England, March 1, 1911, indicates that citrate soluble phosphoric acid has about nine-tenths of the fertiliser value of water soluble phosphoric acid). While this is true of phosphates, the same view is not taken of potash-bearing substances, since practically all of the potash carriers used in agriculture are water soluble. The potash in the ordinary soil minerals is almost entirely insoluble in water, and but slightly soluble in the mineral acids, but if the potash present could be converted into a citric soluble form there seems to be no reason why it should not be considered as available to crops as citric soluble phosphoric acid.

During some investigations carried on in this laboratory on the possibilities of rendering the slags from the iron and steel industries available for fertiliser purposes, attempts were made to fuse together mixtures of felspar and phosphatic limestone with a view to obtaining both the potash and phosphoric acid present in an "available" form (*Bul.* 95, Bureau of Soils, U.S. Dept. of Agr., 1912). Mixtures containing various proportions of these two substances were ignited at temperatures ranging from 1200 to 1400° C., but only viscous fusions were obtained, and the potash and phosphoric acid in none of these were soluble in 2 per cent citric acid, the solution conventionally employed to determine the availability of phosphoric acid in basic slag.

The failure to obtain liquid fusions was at the time attributed to the absence of iron or manganese, or both, in the mixtures, since it is well known that these elements impart fluidity to slags in the manufacture of iron and

steel. Subsequent experiments have proved that such was the case, for on the addition of small quantities of these two elements to certain mixtures of felspar and phosphatic limestone liquid fusions were obtained, and these were found to contain both phosphoric acid and potash in a citric soluble form.

In Table I. is given the composition of the materials used in the experiments:—

TABLE I.—*Composition of Felspar and Phosphatic Limestone used.*

Material (per cent)	Felspar	Phosphatic limestone
SiO <sub>2</sub> .. .. .	65.7	32.4
Al <sub>2</sub> O <sub>3</sub> .. .. .	18.4	—
CaO .. .. .	—	37.1
K <sub>2</sub> O .. .. .	13.7	—
Na <sub>2</sub> O .. .. .	2.2	—
P <sub>2</sub> O <sub>5</sub> .. .. .	—	20.0
CO <sub>2</sub> .. .. .	—	10.5

The above materials were mixed in various proportions, and small amounts of hematite and manganese dioxide were added. Each mixture was then placed in a graphite crucible and heated in a muffle furnace until fusion took place. The melts were then cooled, finely ground, and analysed for phosphoric acid and potash (both total and citric soluble).

It was found that while citric soluble potash can be readily obtained by heating various mixtures of felspar and phosphatic limestone over a wide range of temperatures, the limits within which the maximum yields of citric soluble phosphoric acid are obtained are quite narrow, both in respect to the proportion of the ingredients in the mixture and the length of time of heating.

The percentages of the ingredients used in the various mixtures before ignition and the composition of the melts are given in Table II.:—

TABLE II.—*Proportions in which Ingredients were Mixed and Analysis of Melts obtained.*

	Sample No.			
	25 S.	28 S.	33 S.	31 S.
Amount of material used (per cent)—				
Felspar .. .. .	42.8	37.5	46.8	37.5
Phosphatic limestone ..	42.8	50.0	37.5	42.5
Fe <sub>2</sub> O <sub>3</sub> .. .. .	8.6	7.5	9.4	12.5
MnO <sub>2</sub> .. .. .	5.7	5.0	6.3	7.5
Analysis of melts (per cent)—				
P <sub>2</sub> O <sub>5</sub> soluble in citric acid	2.12	1.50	7.22	5.80
Total P <sub>2</sub> O <sub>5</sub> .. .. .	9.76	11.40	7.21	9.13 (a)
K <sub>2</sub> O soluble in citric acid	6.56	5.32	6.50	4.50
Total K <sub>2</sub> O .. .. .	6.82	5.68	6.48	5.26

Properties of fusion .. .. Slightly viscous. Liquid.

(a) Not determined by analysis, but calculated from the quantity of felspar added.

Table II. shows that nearly all of the potash present after fusing the various mixtures was soluble in 2 per cent citric acid, but in only one case (33 S) was the total phosphoric acid present after ignition soluble in this same medium.

Further investigation showed that both the quantity and solubility of the phosphoric acid remaining in this melt was greatly influenced by the temperature and length of time of heating. In order to test the effect of these two factors on the composition and nature of the melt, this mixture (33 S) was heated for various periods of time and at several different temperatures. The melts thus obtained were cooled, ground, and analysed. The results of these analyses are given in Table III.

It is shown in Table III. that when the mixture was heated to 1200° C. for about twenty minutes the fusion was not complete, and only a little more than 21 per cent

of the total phosphoric acid present was citric soluble; over 88 per cent of the potash, however, was soluble in the same medium. Upon raising the temperature to 1400° C. and maintaining it there for twenty minutes the fusion became quite fluid, and although small amounts of potash and phosphoric acid were lost through volatilisation, the remainder of these ingredients was entirely soluble in 2 per cent citric acid. After heating the mixture for one hour longer at the same temperature, almost 50 per cent of the phosphoric acid and more than 15 per cent of the potash were volatilised, and upon heating for three hours more the phosphoric acid was still further reduced.

TABLE III.—*Properties and Analyses of Melts obtained by heating together Phosphatic Limestone and Felspar with small amounts of Hematite and Manganese Dioxide.*

	Sample No			
	33 SA.	33 SB.	33 SC	33 SD
Temperature of melt (°C.)	1200	1400	1400	1400
Time of heating (minutes)	20	40	100	280
P <sub>2</sub> O <sub>5</sub> (per cent)—				
Citric soluble	1.82	7.22	2.50	1.20
Total	8.50	7.21	3.76	2.88
K <sub>2</sub> O (per cent)—				
Citric soluble	5.98	6.50	Lost.	Not deter.
Total	6.76	6.48	5.48	Do.
Properties of fusion	Viscous.	Liquid.	Less Viscous.	liquid.

The sample richest in citric soluble phosphoric acid and potash (33 SB) was submitted to a microscopic examination by Mr. W. H. Fry, of this Bureau. It was found to be isotropic, and possessed all the external characteristics of a glass.

This was to be expected, however, since the melt was cooled too rapidly to allow of its crystallisation.

(To be continued).

## WELSH NOTES.

(By Our Special Correspondent).

May 15, 1915.

THE trade report of Swansea Harbour for April, which was read this week at the monthly meeting, was a melancholy document, showing as it did a wholesale shrinkage in the exports and imports, the former to the extent of 11 per cent and the latter 7 per cent, or a gross reduction of 43,000 tons. The principal decreases in the exports were as follows:—Tar and pitch 4600 tons, calamine 10,000 tons, steel bars and billets 3000 tons, cement 1000 tons, pyrites 3700 tons. The only articles which materially increased were copper ore 1760 tons, and iron ore 16,000 tons. Patent fuel also showed an increase of 10,000 tons. In regard to the staple manufacture, the tinplate trade, the shrinkage from 34,911 tons to 27,198 tons, was almost entirely attributable to the war, Germany's import of 2087 tons and Roumania's of 4060 tons having disappeared.

There has been great activity at the Swansea blast furnaces during the week, and outputs considerably increased at all the steel works, although there was a shortage of men. The demand for copper continued on a large scale. All refineries were working at the highest pressure. There was some depression in one section of the tinplate trade during the week. The tin and sheet mills and the bar-rolling mills at the Upper Forest Works were idle all the week owing to a dispute. All spelter factories were kept very busy, and the lead-pipe works and safety-fuse factory had a particularly good run. Experimenting departments were going on well at the metal-extraction works, and a splendid trade passed at the Mond Nickel Works. Sulphuric acid factories in the Swansea Valley are going

fairly well, but the demand for vitriol continues on a small scale.

Dowlais Works are very busy, almost every department working at high pressure over the week-end. The blast furnaces produced crude molten iron for the steel converters, and pig iron for stock, &c. The Bessemer and Siemens furnaces are working busily all through. The Goat Mill had a very heavy period on large and heavy patterns of steel rails, billets, and steel sleepers, besides a quantity of square bars of steel and some tin bar. The Big Mill was engaged on lighter materials, such as sole-plates, fish-plates, &c.

The patent fuel works at Port Talbot are working at very high pressure, and the copper works are calling for every available man to deal with some large naval contracts. Tinplates in Port Talbot are experiencing their share of the general slump, only 218 tons being exported last week. I have it on the most reliable authority that negotiations have been completed in connection with the erection of extensive blast furnaces, sheet mills, and by-product works on a site adjacent to the old Port Talbot Copper Works. This project, which is estimated to cost some hundreds of thousands of pounds, has been held in abeyance for some months in consequence of certain technicalities arising in the process of negotiations. These points, I now understand, have been definitely settled, and the scheme will be proceeded with at an early date.

There is to be a probable further development of the important extensions to the Ebbw Vale Steel and Iron Works, which were started last week, for it is now stated that, at the request of the Government, more new plant is to be put down to extract benzol, which yields a chemical necessary in the production of high explosives. This plant has yet to be erected, but it is noteworthy that the Government has seized the opportunity of securing an output of this important product such as will be obtainable from so large an installation as that of the Ebbw Vale Company.

The death took place during the week-end of a well known figure in Welsh chemical trade circles in the person of Mr. D. J. Owen, Ferriell Green, Llansamlet. The deceased gentleman was employed as chemist and assayer at the Swansea Vale Spelter Works, and was very deeply respected in the locality. He took an active interest in the social and religious life of Llansamlet, and it is a sad coincidence that his daughter, the only child, was married but a few days prior to his death.

The death took place at Llanelly Hospital on Tuesday of Frank Groves, Frederick Street, who on the Wednesday previously sustained terrible injuries by falling into a tank of vitriol. Groves was removing a cradle of tinplates from the acid tank to the water when he missed his footing and fell into the acid.

May 22, 1915.

There was some improvement in the trade of Swansea Port during the past week, although a loss of 16,000 tons as compared with the corresponding period last year was registered. Patent fuel exports were very satisfactory here as were they also at Port Talbot. Imports included 148 tons of copper ore from France and also 2287 tons steel scrap from the same country; 2310 tons of blend ore from Spain, 1440 tons of copper ore and 6200 tons of iron ore from Newfoundland. Tinplate shipments were as follows:—77,825 boxes—84,377 boxes being received from works. Stocks in the dock warehouses and vans 320,481 boxes, compared with 313,929 boxes the preceding week and 268,161 boxes the corresponding week last year.

There was no increase in the volume of trade in the Swansea Valley, although great pressure continued at the blast furnaces, and the steelworks collectively showed fair activity. The copper industry was still very busy, but the tinplate trade remained quiet. All the spelter establishments are in full swing, and the aggregate production during the past few days has been very heavy. Safety-

fuse and lead-pipe factories are working well, and there was little change at the Mannesmann Tube Works, employment still being heavy. Production at the Mond Nickel Works is still growing, and employment is especially good at the metal extraction departments. Iron and brass foundries and moulders are actively engaged, but a slight decline is experienced at the sulphuric acid factories, due, I am told, to the poor call for vitriol.

A very strenuous period is being experienced at the Dowlais Steel and Iron Works, all departments from the furnaces to the rail-banks being well employed. The Goat Mill turned out during the week steel sleepers, steel rails of heavy pattern, cogging steel and bars, besides some tin bars. The Big Mill was engaged on light tram rails for colliery sidings and underground work, curves and props and fish-plates, for which there was a good amount of pressure.

The war is hitting the Welsh tinplate industry very hardly, and there are many soundly-based fears that much of its export business, upon which it mainly depends, will be captured by its great competitor, the United States. For the four months ending April 30th the total exports of tinplates, terneplates, and blackplates amounted to 143,176 tons, as compared with 194,995 tons in the corresponding period last year, a reduction of 26 per cent. As against this there has been a little increase in home consumption. At present, out of 581 sheets and tinplate mills in the industry about 150 are idle. The price of tinplates is now higher than in the record year of the McKinley boom. The price then was 17s. 6d. per box; the price now quoted is 18s. 3d.

It is the high price of Welsh plates that will give a golden opportunity to American competitors to capture exclusively Welsh business. Wales to-day stands no chance of securing any of the rebate trade. A little while ago the Standard Oil Company entered the market for 220,000 boxes to be used in the American export trade, and on account of the rebate imported plates would be practically tariff free. Welsh makers, however, on account of the low prices reigning in America were entirely out of running as the order was snapped up by an American independent plant at about 12s. per box, 100 lbs.

Three days after I wrote in these notes last week, of the new blast furnaces and steelwork plant to be installed at Port Talbot, an official announcement was made at Birmingham. The new coke ovens and by-product plant alone will cost £500,000, although it has been definitely decided that building operations will not be proceeded with until peace is in sight.

These important developments are supplemented by the scheme of another company—the Atlas Coke and Patent Fuel Company—which is connected with the Cribbwr Vawr Collieries and will utilise a site adjoining that of Messrs. Baldwin's, at the Port Talbot Docks, for the purpose of establishing coke ovens. It is intended in the by-product works to extract all by-products down to tar and the surplus gas will be used for the generation of electric power.

It is interesting to note that the system adopted in the new steelworks will be identical with that in use at Landore, utilising the invention of Mr. Cast of carrying the molten pig iron direct from the blast furnaces to the steel furnaces and converting it into steel by practically one process.

The large new Technical College which Swansea has in view is a source of much anxious speculation as to whether it will receive any encouraging grants for the purpose of engineering and chemical instruction. There is no doubt that a magnificent system of technical training is needed in South Wales. Many clever young men have been debarred, by expense, from taking advantage of the English schools, and it is only reasonable to believe that science has lost thereby many a brilliant adornment. There are good reasons, however, for believing that all this is to be changed in the very near future, for Wales has awakened to its need, and Swansea, in particular,

supported by a band of practical enthusiasts, is determined to bring about a new order of things.

Sir Alfred Mond, M.P. for Swansea, has been giving the Government the benefit of his chemical knowledge on the subject of asphyxiating gas, and is at the present moment sitting on a Committee which is considering the subject. He is, by the way, one of the largest manufacturers of chlorine in the world.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, May 13, 1915.*

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*The Development of the Thymus, Epithelial Bodies, and Thyroid in the Vulpine Phalanger (Trichosurus vulpecula).*" By ELIZABETH A. FRASER and Prof. J. F. HILL, F.R.S.

"*Some Observations on the Development of the Thymus, Epithelial Bodies, and Thyroid in Phascogaster, Phascogaster, and Termites.*" By ELIZABETH A. FRASER.

"*Measurement of the Specific Heat of Steam at Atmospheric Pressure and 104.5° C.*" By J. H. BRINKWORTH. With a Preface by Prof. H. Callendar, F.R.S.

The measurement of the specific heat of steam in the immediate neighbourhood of 100° C. permits extreme steadiness in the conditions of observation, and is important as a starting-point for the investigation of the variation of the specific heat with pressure and temperature, but presents special difficulties owing to the possible presence of water in suspension when the superheat is very small.

The majority of determinations, such as those of Regnault (125 to 225° C.), and Holborn and Henning (110 to 270° C.), have been made with highly superheated steam, and throw little light on the value near 100° C. Those of Knoblauch and Jacob, and Knoblauch and H. Mollier, when extrapolated towards saturation, appear to indicate a very rapid increase in specific heat near the saturation-point.

The theory of the variation of specific heat with pressure is discussed in the preface in relation to some experiments by the Joule-Thomson method, the results of which were published in a previous communication. It is shown that the presence of only half-a-millionth of a gram. molecule of salt per gram. of steam is sufficient to raise the apparent specific heat by 10 per cent at 103° C., and that previous measurements near saturation were probably affected to a slight extent by this source of error.

Special precautions were taken in the investigation to secure pure dry steam, and the conditions of experiment were varied widely, especially with regard to external heat-loss. By using a silvered jacket of silica maintained at a high vacuum the loss was reduced to about a tenth of that in previous experiments, and amounted to only two or three parts in 1000 of electric energy supplied.

The final result found was—

$S = 2030$  joules per gram. per 1° C., at 760 mm. and 104.5° C.,

which is equivalent to 0.485 mean calories under the same conditions, and is in good agreement with Regnault's result at 175° C. if allowance is made for the small variation deduced from the experiments by the throttling method.

"*Thermal Properties of Carbonic Acid at Low Temperatures.*" (II.). By C. F. JENKIN and Dr. R. PYE.

This is a continuation of the paper on the same subject published in the *Phil. Trans.*, A, cxxviii., 67. It contains a description of (1) a series of measurements of the total

heat of  $\text{CO}_2$  gas from which the specific heats are deduced; (2) a few re-measurements of the total heat of liquid  $\text{CO}_2$ ; and (3) a series of throttling experiments on  $\text{CO}_2$  gas.

By means of the first series the  $\theta\phi$  chart, part of which was drawn in the former paper, is extended over the superheated gas area; its accuracy is then checked by means of the throttling experiments. Graphic methods are described for plotting the results of throttling experiments, and thereby checking the specific heats of the gas and position of the gas-limit curve.

Finally, an  $\text{I}\phi$  chart is constructed for  $\text{CO}_2$  based on the measurements described in both papers. To assist in the construction of this chart a series of theorems connecting the total heat  $\text{I}$  with the other variables  $p$ ,  $v$ ,  $\theta$ , and  $\phi$  are worked out, and their use in checking the accuracy of  $\text{I}\phi$  charts for any substances is explained.

The authors hope that the new  $\text{I}\phi$  for  $\text{CO}_2$  chart, which extends and corrects Mollier's, may be of some technical value in the refrigeration industry.

## NOTICES OF BOOKS.

*The Absorption Spectra of Solutions as Studied by means of the Radio-micrometer.* By HARRY C. JONES and Collaborators. Washington, D.C.: The Carnegie Institution. 1915.

THE working bearing directly or indirectly on the solvate theory of solution which has been done in the Johns Hopkins Laboratory during the last fifteen years has been brought together in this monograph. The first paper describes the work on the absorption spectra of solutions done by Dr. Shaeffer and Mr. Paulus. The radio-micrometer used for studying the absorption spectra quantitatively consisted of a thermo-electric junction attached to a loop of non-magnetic wire, the whole being suspended in a magnetic field. A differential method of determining the transmission of light was employed, and special cells were constructed for the purpose. The work of earlier investigators showed that combined water has less power to absorb light than free water, and the authors have now found that solutions of some non-hydrated salts are about as transparent as pure water, except at the bottoms of the absorption bands, where they are more opaque. Solutions of hydrated salts have generally greater transparency than pure water at the centres of the absorption bands. The second chapter contains the report of Dr. Leslie D. Smith's work on the conductivities, temperature coefficients of conductivity, dissociations, and constants of some organic acids in aqueous solutions, the object of the investigation being to obtain more data over a wide range of temperature and dilution, to improve methods and discover new relations. Most of the earlier work has been confirmed, and some fresh results have been obtained. In the next paper work on the conductivity of certain organic acids in ethyl alcohol is described. For the purposes of this investigation different types of cells had to be employed owing to the high resistances of alcoholic solutions. The investigation was of a preliminary nature only, but some very important results were obtained and certain anomalies in the variation of the conductivity were observed. It is found that with the organic acids the conductivities in alcohol are often several hundred times smaller than in water. The conductivity and viscosity of solutions of potassium iodide and sodium iodide in mixtures of ethyl alcohol and water were studied by Dr. Wightman, Dr. Davis, and Mr. Holmes, and some improvements in methods of determining them were suggested; in general the results of previous workers were confirmed. Rubidium salts in mixtures of acetone and water, and also rubidium and ammonium salts in ternary mixtures of glycerol, acetone, and water have also been investigated. The conductivities of the ternary solvents indicate that water and acetone act as dissociating agents in glycerol. Temperature coefficients of fluidity are larger than for con-

ductivity, as in binary solvents, and the formation of solvates is a possible explanation of the difference between these coefficients. The investigation emphasises the already known fact that fluidity probably outweighs all the other factors affecting conductivity. The last chapter of the book consists of the monograph recently noticed in the CHEMICAL NEWS. The lines of evidence in favour of the solvate theory are summarised in it and discussed, and the significance of the theory is well explained.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx. No. 16, April 19, 1915.

**Benzofulvanol and Benzofulvene.**—V. Grignard and Ch. Courtot.—Benzofulvanol can be prepared by the action of the magnesium derivative of indene on trioxymethylene. The magnesium compound is precipitated in toluene and washed with anhydrous ether, in which it is afterwards suspended. The calculated quantity of dry trioxymethylene is then added, and the mixture is heated with a reflux condenser for about five hours in an atmosphere of hydrogen. The liquid is hydrolysed over ice with ammonium chloride and ammonia, the ethereal solution is dried, and the ether is distilled off at a temperature not exceeding  $50^\circ$ . The residue consists of benzofulvanol, which can be purified by distillation *in vacuo*. It appears to be the  $\alpha$ -alcohol, and it can be dehydrated quantitatively by Senderens' catalytic method *in vacuo*, the product being benzofulvene, which readily polymerises giving a vitreous mass like colophane.

**Theory of Oscillation of the Indene Double Bond.**—Ch. Courtot.—By the action of benzyl chloride upon the magnesium derivative of indene the author has shown that the mono-substituted indenenes are capable of existing in the free state in the  $\alpha$ - and  $\gamma$ -forms, the  $\alpha$ -form being readily converted into the other by the action of alkalis. This phenomenon of isomerisation has made it impossible, up to the present, to isolate the  $\alpha$ -derivatives.

## NOTES AND QUERIES.

**Vanillin and Benzaldehyde.**—The favour is requested of the address of an English manufacturer of vanillin and chlor free benzaldehyde. These chemicals I have imported from Germany, but would like to get some from England.—A.L.R. AVI P.

## MEETINGS FOR THE WEEK.

TUESDAY, June 1st.—Royal Institution, 3. "The Evolution of Steel—Influence on Civilisation," by Prof. J. O. Arnold, F.R.S.

WEDNESDAY, 2nd.—Society of Public Analysts, 8. "Estimation of Starch in Cocoa by the use of Taka Diastase," by C. Revis and H. R. Burnett. "Volumetric Estimation of Ferroryanides," by B. Campbell. "Corean Beeswax," by S. Ueno. "Determination of  $\beta$ -Naphthol in Lysol and similar Compounds," by R. Bodmer. "Composition of Dutch Cheese," by J. J. L. van Ryn.

THURSDAY, 3rd.—Royal Institution, 3. "Methods of Presenting Character in Biography and Fiction," by Wilfrid Ward.

Royal Society. "Soil Protozoa and Soil Bacteria," by E. J. Russell. "The Chromosome Cycle in Coccidia and Gregarines," by C. Dobell and A. P. Jameson. "Influence of Gases on the Emission of Electrons and Ions from Hot Metals," by O. W. Richardson. "Shapes of the Equipotential Surfaces in the Air near long Buildings or Walls and on their Effect on the Measurement of Atmospheric Potential Gradients," by C. H. Lees. "The Band Spectrum associated with Helium," by J. W. Nicholson.

Chemical, 8.30. "Thermal Study of the Carbonisation Process," by H. Hollings and J. W. Cobb. "Properties of Cold-worked Metals—Part I., The Density of Metallic Filings," by T. M. Lowry and R. G. Parker.

FRIDAY, 4th.—Royal Institution, 9. "Radiations from Exploding Atoms," by Prof. Sir Ernest Rutherford, F.R.S., &c.

SATURDAY, 5th.—Royal Institution, 3. "Mary Queen of Scots," by Prof. R. S. Rait.



# THE CHEMICAL NEWS.

VOL. CXI., No. 2897.

## ANILINE DYES.

By Mrs. DOUGLAS.

ANILINE dyes were a triumph of chemical ingenuity over natural production. The simple old method of the home-dyers was to extract his colours from the plants, the lichens, and the barks of trees that grew about his doors.

The very first aniline preparation was made by Unverdorben in 1826, and was obtained by dry distillation from indigo. Curiously enough to-day the indigo plant is the one that has been most thoroughly superseded, because aniline indigo can be obtained so much more cheaply. So in manufacturing this colour Germany has practically killed one of India's finest native industries, and it seems to us that this would be a most excellent time to revive it. There has, of late years, been a considerable reaction in favour of genuine native herbal dyes. They produced infinitely more artistic shades than the much-vaunted aniline dyes.

This interchange of aniline and indigo shows that they are very nearly related. Aniline takes its name from *anil*, the Portuguese word for indigo.

It was in 1834 that aniline was first produced from coal-tar by Runge. To his preparation he gave the name of *kyanol*, on account of the power he discovered it possessed of producing purple or violet tints when united with bleaching-powder. The next step was taken by Fritsche, who, in 1840, produced a volatile liquid from indigo, and was the first to give it the name of *aniline*, for Unverdorben had called his product *crystalline*. Very soon after another chemist called Zinin brought out a liquid called *bensidam*, reduced from nitrobenzene (a derivative of coal-tar), and Fritsche promptly pointed out that it was practically identical with *aniline*. It only remained for Hofmann, in 1843, to make clear that *crystalline*, *kyanol*, *aniline*, and *bensidam* were all one and the same thing. Thus the genealogy of aniline is complete.

It will be noted that all these discoveries were made by German chemists, but it was an Englishman, Mr. W. H. Perkin, who, in 1856, was practical enough to utilise aniline as a dye. Germans are quick to take a hint, however, and although Britons started the manufacture they were soon out-distanced by foreign competitors, and practically the whole trade passed into German hands.

The first dye produced by Mr. W. H. Perkin was a brilliant and delicate mauve. The aniline dyes rose to the height of their fame in the Victorian era, and are eminently characteristic of it. At first they emulated the petunia and the cineraria in their range of bright but inartistic shades. Of late years they have been marvelously modified and an extremely rich range of shades from sober to gay has been obtained. But wonderful as they are, however, they never satisfy the artistic soul as do the old-fashioned herbal dyes, whose tints seem to come direct from the palette of Mother Nature.

Aniline is a colourless liquid, and is manufactured by the action of hydrochloric acid and iron scraps on nitrobenzene. Lime is added, and the aniline distilled by steam. The different dyes are obtained mostly by combining aniline with various acids. Hofmann, for instance, first produced red by treating aniline with nitric acid. Endless discoveries and adaptations have been made, however, in the use of aniline.

It is one distressing fact that the manufacture of aniline dyes is not a very healthy occupation. Those engaged in it often suffer from headaches and nausea. On the other hand, aniline is of considerable use in the preparation of certain medicines. It may be mentioned that all work-

men are not injuriously affected by aniline; many after a fortnight or so become accustomed to it, and find it quite as healthy as most occupations.

Aniline is one proof of the marvellous properties of coal-tar. No substance has produced a greater variety of useful and beneficial substances. It is said that diamonds can be made from coal-tar oil. Creosote, benzene, and naphthalene are amongst the best known variants of coal-tar.

The whole history of dyes is interesting and romantic. The Eastern nations have ever been artists in colours, and the famous Tyrian purple dates from 1500 B.C. Pliny describes how a single drop of colouring matter was obtained from a sac liquid in the throat of each tiny murex. This liquid was heated with sea-salt exposed to the air, and after a somewhat lengthy although not elaborate process made ready for use. Cochineal is also an animal dye, but the pure indigo and saffron, like all the best dyes, come from comparatively insignificant plants.

## A REVISION OF THE ATOMIC WEIGHT OF LEAD.\*

INVESTIGATIONS have been carried out at the Chemical Laboratory of Harvard College by Gregory Paul Baxter, Thorbergur Thorvaldson, and Fred Leslie Grover upon the atomic weight of lead from different sources.

Very thorough precautions were taken in the preparation and purification of all the reagents and apparatus used, and separate investigations were conducted for the production of lead and silver, nitrates and bromides, and the purification of the lead. The determinations were by the analyses of the bromides.

Two series of determinations were first made, one of twelve and the other of six experiments; the individual values found varied between the limits 207.14 and 207.22, giving a mean of 207.19.

The work was continued by Mr. Grover using both lead bromide and lead chlorides. Elaborate research was conducted on the purification of the lead nitrate from which the bromide was prepared, and the lead was examined spectroscopically. The silver and copper lines were very difficult to eliminate, but the material ultimately used was quite free from these or any other impurities. Two series of determinations were again made, one of nineteen and one of eleven experiments; the variations were between 207.14 and 207.23, giving a mean again of 207.19.

While these investigations were in progress, the exact value of the atomic weight of lead became of considerable importance in connection with the theory of atomic disintegration of the radio-active elements. According to the hypothesis of Fajans (*Ber.*, 1913, xlv., 422) and Soddy (*CHEMICAL NEWS*, 1913, cvii., 97) at least two lead "isotopes" exist, one resulting from the expulsion of five  $\alpha$ -particles from radium with an atomic weight 206, the other resulting from the expulsion of eight  $\alpha$ -particles from thorium with an atomic weight of about 208.3. If ordinary lead is composed of, or contains, these isotopes, in proportions varying with its origin, then its atomic weight might be expected to vary according to its source. Richards and Lambert (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 1329) found that, in accordance with this hypothesis, radio-active lead extracted from radio-active minerals possesses an atomic weight different from that of ordinary lead, and differing also according to the mineral from which it is extracted, a result confirmed by Hönigsmid (*Comptes Rendus*, 1914, clviii., 1786; *Zeit. Elekt.*, xx., 319), M. Curie (*Comptes Rendus*, 1914, clviii., 1676), and Soddy (*Proc. Chem. Soc.*, 1914, xxx., 134). In order to find out whether ordinary lead is subject to similar varia-

\* Abstracted from the *Journal of the American Chemical Society* xvii., No. 5, May, 1915.

tions, seven varieties of inactive lead material from known widely different geographical sources were examined. Not the slightest difference between any of these specimens could be detected so far as analysis of the chloride is concerned. Furthermore, these specimens were found to be spectroscopically identical and none of them were radioactive, so far as could be determined. While the evidence thus obtained is by no means final as to the origin of ordinary lead, it certainly is striking that, if common lead is composed either wholly or in part of isotopes, its composition should be essentially constant.

## THE CHEMICAL INDUSTRIES OF GERMANY.\*

By Prof. PERCY F. FRANKLAND, F.R.S.

(Continued from p. 237).

**Hydrogen Industry.**—The electrolytic production of soda and chlorine is of course attended with the evolution of enormous volumes of hydrogen. At first this gas was allowed to go to waste, but gradually interesting and important uses have been found for it. (1) Dingible balloons, rendered possible by taking advantage of the lightness of the internal combustion engine. One horsepower engine is but little heavier than 1 kilogram. 27,000 cubic metres of hydrogen is required for a modern airship. The balloon sheds are often established near electrolytic soda works, or the gas may be transported in steel cylinders compressed to 150 atmospheres. 500 cylinders containing 2750 cubic metres of gas are placed on one railway wagon, and more than eight such wagon-loads are required for the filling of a single Zeppelin. (2) Auto-genous welding with oxyhydrogen flame. These most important applications of hydrogen were introduced at the beginning of this century by the Chemische Fabrik Greisheim-Elektron. The oxyacetylene flame is now more commonly used. (3) Artificial gems by means of oxyhydrogen flame. Some thirty years ago C. V. Boys succeeded in fusing quartz with the oxyhydrogen flame and then drawing it out into incredibly thin fibres, which have proved of the highest value for certain physical experiments of extraordinary delicacy. The same source of heat was much later, in the nineties, employed by the French investigator, Michaud, to reconstruct rubies from small fragments of this gem. At the beginning of this century Verneuil and Paquier in Paris succeeded in making synthetic rubies. A little later Wild, Miethé, and Lehmann in Germany elaborated methods for producing synthetic corundum, rubies, amethysts, and sapphires, which are manufactured by the Elektrochemische Werke at Bitterfeld. These products are identical in chemical composition and physical properties with the natural gems, and the rarest varieties of these can be obtained at will. Fused alumina (very pure) gives corundum, fused alumina + 2½ per cent chromic oxide gives ruby, fused alumina + magnesia and titanium oxide and ferric oxide gives blue sapphire. These synthetic gems are now manufactured to the extent of about six million carats annually (1 carat = 0.205 grm.), or 1230 kilos., or more than one ton. Experienced connoisseurs can, however, distinguish between the natural and artificial gems, with the result that the former have not diminished in value. Natural rubies or sapphires of 2–4 carats cost £20–£50, and larger stones up to £150, whilst the artificial would only cost 1/500–1/1000 of those mounts.

A still more recent and much more important application of hydrogen is for the hardening of fats, which depends on the transformation of unsaturated into saturated acids by means of hydrogen in the presence of a catalyst (nickel, palladium, &c.).

**Industries connected with Artificial Illumination.**—The world is greatly indebted to Germany for inventions which have largely revolutionised artificial illumination, firstly in connection with gas, and more recently in respect of electric lighting.

Thus, one of the most remarkable discoveries in this domain was that of incandescence gas lighting, which was made by the Austrian Count Dr. Carl Auer v. Welsbach, of Rastarsfeld, in Styria, as the result of lengthy, laborious, and ingenious researches. The now so familiar gas mantles are prepared by the ignition on the cotton frame of a mixture of thorium nitrate, 99; cerium nitrate, 1 per cent.

The source of these rare earths is monazite sand, the elaboration of which has become a very important industry depending on fractional crystallisation, which already many years ago was brought to such a high pitch of perfection in the laboratory of Sir William Crookes. Out of this monazite sand, Otto Hahn in 1910 succeeded in extracting mesothorium, and the process is carried out on a large scale at the works of Dr. O. Knofler and Co., at Ploetzensee, near Berlin. Radium bromide is worth about £17 a milligram., mesothorium about £7 10s. a milligram. The mesothorium is only present in the monazite sand in extremely small proportion, about 1 part in 150 million parts of the mineral.

I may also refer to Auer metal, a preparation of iron (Fe 30 per cent) containing cerium, which sparks when scratched with hard steel, and which is familiar as a substitute for matches.

**Electric Light Metallic Filaments.**—Another outlet for the use of hydrogen has been in reducing the rare metals osmium (m. pt. 2500° C.), tantalum (m. pt. 2300° C.), and tungsten (m. pt. 2850° C.).

In 1903 the Auer Company showed that the carbon filament of incandescence electric lamps could be replaced by an osmium filament with an economy of 50–60 per cent of current. In 1905 Siemens und Halske showed that a tantalum filament was cheaper and more advantageous, and in 1906 that the tungsten filament was even still better. Tungsten occurs in sufficient quantity in nature as wolframite (iron tungstate) and scheelite (calcium tungstate) to enable the metal to be now sold as filament metal for 6s.—7s. a kilogram.

	1911.	1912.
Metallic filament electric lamps..	47,211,892 pieces	76,185,721 pieces
Carbon filament electric lamps..	24,791,196 "	20,975,348 "
Incandescence gas mantles ..	126,050,954 "	135,320,173 "
Arc-lamp carbons	10,740,025 kilos.	11,093,154 kilos.

Some idea of the enormous and increasing scale on which the incandescence lighting manufacture is carried on in Germany may be gathered from the figures given above.

According to V. B. Lewes, the consumption of gas mantles in 1912 was:—Germany, 100,000,000; America, 60,000,000; England, 38,000,000; France, 16,000,000; Belgium, 3,500,000; Italy, 3,000,000; Russia, 1,500,000.

The special tax imposed in Germany on lighting apparatus realised from the above sources in 1912 was £800,000. This remarkable tax was one of those extraordinary financial expedients resorted to by Germany during recent years to provide the wherewithal for the stupendous national effort to subjugate Europe of which we are the witnesses to-day.

**Ammonia.**—Of the commoner inorganic chemicals which are produced on the largest scale, one of the most important is ammonia, which has for so many years been obtained as a by-product in the manufacture of coal gas.

So backward was this industry in Germany that actually even as late as 1874 the ammoniacal liquor from their gas works was run to waste. All the more remarkable is the state of affairs to-day, as betrayed by the following figures. The world production of ammonium sulphate

\* Meeting held at Birmingham University on March 4, 1915. From the *Journal of the Society of Chemical Industry*, xxxiv., No. 7.

was 210,000 tons in 1890, 500,000 tons in 1900, and 1,330,000 tons in 1912. Germany's production of ammonium sulphate in 1912 was about 370,000 tons.

	1888.	1912.
	Tons.	Tons.
Chili saltpetre (a) .. ..	225,000	650,000
Sulphate of ammonia .. ..	50,000	500,000
Superphosphate .. ..	250,000	1,800,000
Basic slag .. ..	250,000	2,200,000
Crude potash salts .. ..	160,000	3,000,000
Lime .. ..		800,000
Other manures .. ..	500,000	500,000
Total value .. ..		£30,000,000

(a) The total import of Chili saltpetre into Germany in 1912 was 800,000 tons, of which only 150,000 tons was used for manufacture of potassium nitrate and nitric acid.

The principal use of sulphate of ammonia is as a nitrogenous manure, as which it competes with Chili saltpetre: they may be taken as of equal money value per unit of nitrogen. In this connection Germany's manure bill is interesting (see table above).

It is the ambition of the Germans, firstly, to make themselves independent of the industrial products of other countries, and, secondly, to produce in excess of their own needs and to impose this surplus on the rest of the world. Thus, they pride themselves on displacing more and more of the foreign Chili saltpetre by home-made sulphate of ammonia, and in 1911 they used in agriculture 75,000 tons of ammoniacal nitrogen against 70,400 tons of foreign saltpetre-nitrogen. This partial success they look forward to making complete and decisive by developing new methods of producing ammoniacal nitrogen and nitrates, which can be carried out in Germany. Of such methods there are already two in operation, and they are associated with that great problem which confronts mankind as a whole. How to supply the combined nitrogen which will be necessary to build up the food-stuffs for the teeming millions of the future after the deposits of Chili saltpetre are exhausted? This is the same problem as that of fixing the nitrogen of the air, which long ago, before anything was known of nitrogen at all, man had solved empirically by growing leguminous plants in the rotation of his crops, thereby increasing the fertility of the soil, although the mechanism of this time-honoured procedure was only experimentally demonstrated in the last decades of the nineteenth century by the German investigators, Willfahrt, Hellriegel, and Nobbe.

**Fixation of Atmospheric Nitrogen by Inorganic Means.**—This has been successfully accomplished by:—

(1). The Birkeland and Eyde electric furnace and the Schönherr electric furnace of the Badische Anilin und Soda Fabrik. These are simply realisations on the industrial scale of laboratory experiments made by Cavendish 30 years previously. This method is applicable only in Norway, or other countries where abundance of water power renders the production of cheap electrical energy possible. It is being carried on by an international company at Notodden, in Norway. They propose to use 300,000 horse-power, capable of yielding 150,000 tons lime-saltpetre (15–20 per cent N), or about one-twelfth of the total amount of Chili saltpetre used by the world. Germany possesses but little water power, so that this process is of only indirect interest in connection with German chemical industry.

(2). Fixation of nitrogen by calcium carbide at high temperatures. This discovery was made by the German chemists Frank and Caro. £5,000,000 capital is already embarked in this industry by various companies of Europe and America. About 220,000 tons is produced annually, about one-quarter of which in Germany. The crude calcium cyanamide (about 20 per cent N) may be used

directly as a nitrogenous manure, or may be made to yield ammonia. The production of calcium carbide involves the use of the electric furnace, and hence cannot be carried on economically on a very large scale in Germany owing to the limited water power available.

(3). Combination of nitrogen and hydrogen at higher temperature, and especially under high pressure. The long known fact that the reaction,  $N_2 + 3H_2 = 2NH_3$ , is realised to a very small extent at high temperatures has been investigated in recent years by Haber and Le Rossignol at Karlsruhe, and, guided by the principles of modern physical chemistry, Haber has elaborated, after overcoming extraordinary technical difficulties, an industrial process which promises to be of great importance in the future. The most advantageous conditions were found to be:—Pressure, 200 atmospheres; temperature, 500° C.; catalytic agent, osmium, uranium, &c.

Production of ammonia by the Haber process has been carried out on a commercial scale by the Badische Anilin Company since the summer of 1913, and a plant capable of yielding 130,000 tons of sulphate of ammonia per annum was to have been ready during the present year. Inasmuch as the German Colour Syndicates have severed their connection with the Norwegian nitre undertaking, it would appear that they regard the Haber ammonia process as being more likely to be capable of capturing the inorganic nitrogen market of the world.

This synthetic production of ammonia obviously involves cheap hydrogen. I have already referred to electrolytic hydrogen, but there are cheaper sources. Thus water-gas contains theoretically equal volumes of hydrogen and carbon monoxide; the carbon monoxide (b. p. -192° C.) can be removed by liquefaction from the hydrogen (b. p. -253° C.). Similarly the nitrogen required for the process is obtainable from the fractional distillation of liquid air. The synthesis of ammonia thus dovetails with the possibilities of cheap low temperature production, for which the world is so largely indebted to the German engineer, Carl von Linde, of Munich.

The German ambition to make their combined nitrogen at home does not stop at the production of synthetic ammonia, for there are still large requirements in respect of nitrates (Germany produces upwards of £1,500,000 of nitric acid annually from Chili saltpetre), which have to be satisfied from foreign sources. They hope, however, to fill this gap in the home production of combined nitrogen by utilising a reaction discovered by Kuhlman as long ago as 1839 (*Ann. Chem. und Pharm.*, 1839, xxix., 280), in which ammonia and air burn to nitric acid in the presence of platinum as a catalytic agent.

**Potash Salts.**—Germany appears to be alone in possessing vast deposits of potash salts, whilst the enormous value of these to agriculture was first demonstrated by Liebig and made public by him in his "Application of Chemistry to Agriculture and Physiology" in 1840. This work may without question be regarded as the foundation-stone on which agricultural chemistry has been raised. The celebrated deposits of potash salts were accidentally discovered in 1857, when boring for rock salt at Stassfurth, near Magdeburg, in Prussia. Their industrial exploitation on an ever increasing scale was begun in 1861 by Grüneberg and Adolf Frank. In 1861 the production of crude potash salts was 2000 tons; in 1912, 11,000,000 tons, worth £8,800,000. Ninety per cent is used as manure (about one-third in Germany itself), and 10 per cent in industries (about two-thirds being worked up in Germany for carbonate, caustic, nitrate, alum, chromate, and chlorate, &c.). America is now experimenting with a view to obtaining potassium chloride from feldspar by the method used in the laboratory for determining alkalis in insoluble silicates, and which consists in heating the silicate with a mixture of lime and calcium chloride. Whether it has any commercial future remains to be seen.

This is a matter of prime importance in the United States, as potash salts are there used on an enormous

scale, especially for agriculture; thus they consumed in 1900 Stassfurth potash salts worth £840,000; in 1910 £2,440,000; and in 1911, £3,040,000 (Molinari).

(To be continued).

## THE PRODUCTION AND FERTILISER VALUE OF CITRIC-SOLUBLE PHOSPHORIC ACID AND POTASH.\*

By WM. H. WAGGAMAN,  
Scientist in Investigation of Fertiliser Resources.

(Concluded from p. 262).

### Solubility of the Potash of the Slag in Water saturated with Carbon Dioxide.

THE fact that the phosphoric acid of basic slag is fairly soluble in water saturated with carbon dioxide is taken as an added proof of its availability under soil conditions. It was thought advisable, therefore, to test the solubility of the potash in the slag product (33 SB) in this same medium, comparing this solubility with that of the potash in felspar.

Considerable work has been done on the so-called solubility of orthoclase in water and in various other solvents (Roger Brothers, *Am. Journ. Sci.*, 1848, ii., 401; A. Daubrer, "Etudes Synthétiques de Géologie Expérimentales," 1879, 268; F. W. Clarke, *Journ. Am. Chem. Soc.*, 1898, xx., 739; Lemberg Inaugural Dissertation Dorkat, 1877; Cameron and Bell, *Bul. 30*, Bureau of Soils, 1905; Cushman and Hubbard, *Bul. 28*, Office of Public Roads, 1907; see also Cameron, *Proceedings Eighth International Congress of Applied Chemistry*, New York, 1912, xv., 43 *et seq.*). It is recognised, however, that this mineral has no definite solubility in water, but the dissolved material undergoes practically complete hydrolysis or decomposition, the amount of this decomposition being considerably affected by the fineness of the mineral, the method of grinding it (whether wet or dry), the quantity and temperature of the water used, and the length of time the water is allowed to act.

In Table IV. the apparent solubility of felspar in pure water and in water saturated with carbon dioxide as determined by several investigators is given. Few of these results are comparable, owing to the different conditions under which the experiments were conducted, but they are of interest in showing what widely divergent results are obtained by varying these conditions.

TABLE IV.—Solubility of Felspar in Water and in Water saturated with CO<sub>2</sub>, as determined by various investigators.

Investigator.	Amount of felspar used.	Amount of water used.	Time of contact.	Amount of K <sub>2</sub> O dissolved from felspar.	Amount of K <sub>2</sub> O in solution.
	Grms.	Grms.		P.c.	Parts per mil.
Daubrer (a)	3000	5000	192 hours	0.420	2520.0
	2000	3000*	240 hours	0.013	90.0
Cameron and Bell (b) ..	2	1000	14 months	0.085	1.7
Cameron and Bell (b) ..	2	1000*	"	0.125	2.5
Cushman and Hubbard (c)	25	100	Not given	0.100†	250.0†
Cushman and Hubbard (d)	25	100	Not given	1.280†	3200.0†

(a) Triturated in revolving cylinder.

(b) Allowed to stand in contact with water.

(c) Mineral ground while dry.

(d) Mineral ground wet.

\* CO<sub>2</sub>

† Total residue

In the experiments for comparing the solubility of the potash in 33 SB with that of felspar, a large quantity of the slag product was first prepared and ground to pass a 200-mesh screen. On analysis this material showed the following composition:—

	Per cent.
K <sub>2</sub> O citric soluble .. .. .	5.14
K <sub>2</sub> O total .. .. .	5.43
P <sub>2</sub> O <sub>5</sub> citric soluble .. .. .	6.32
P <sub>2</sub> O <sub>5</sub> total .. .. .	6.31

Two samples of this slag, of 25 grms. and 0.25 grm. respectively, and the same quantities in weight of felspar (ground equally fine), were placed in platinum-lined brass cylinders, 100 cc. of water were added to each, and carbon dioxide under an average pressure of 1½ atmospheres was passed through the solutions for one week. At the end of that time the amount of potash dissolved from each sample was determined by analysis of the solutions. The results of these analyses are given in Table V.

TABLE V.—Solubility of the Potash in the Slag Product (33 SB) in Water saturated with Carbon Dioxide, compared with that of the Potash in Felspar.

Material used.	Amount of material used.	Amount of water employed.	Potash dissolved.	
			Potash in solution.	Percentage of total potash in sample.
	Grms.	Cc.	P.p.m.	
Felspar .. ..	25.00	100	127.5	0.36
Do. .. ..	0.25	100	4.7	1.37
Slag (33 SB) ..	25.00	100	150.0	1.11
Do. .. ..	0.25	100	11.9	8.76

In the case where large samples (25 grms.) of slag and felspar were used the resulting solutions differed but little in respect to their potash content, but considering the fact that the sample of slag contained less than one-half as much potash as the felspar, the percentage of potash dissolved from the former was nearly four times as great. Moreover, while no quantitative determinations were made of the total solids in solution, the amount dissolved from the slag was apparently many times greater than that dissolved from the felspar.

In the case where only 0.25 grm. samples of the two substances were used, the slag yielded a solution nearly three times as strong (in respect to potash) as the felspar, and when the quantity of potash in the two substances is considered the percentage dissolved from the slag was nearly seven times greater.

### Results of Pot Tests with Slag Fertiliser.

Although the solubility of the potash and phosphoric acid in the slag product was indicative of its agricultural value, it was thought advisable to test its merits by actually growing plants in soils treated with this material, and comparing their growth with that of plants grown under similar conditions in the same soils untreated and treated with well known potassic and phosphatic fertilisers.

The experiments were conducted by Mr. J. J. Skinner, of this Bureau. The wire basket method described in Circular 18, Bureau of Soils, was employed, using wheat seedlings.

Three types of soil were used, namely, the Carrington silt loam from Wisconsin, the Hagerstown loam from Pennsylvania, and the Volusia silt loam from New York. These soils are described in Bulletin 96 of this Bureau as follows:—

"The Carrington silt loam consists of a dark brown to black silt loam, having an average depth of about twelve inches. The subsoil is a yellowish-brown to pale yellow silty clay loam or silty clay. The topography is mainly level to undulating. The soil represents a residual stratum derived from glacial till. The type is admirably

\* Bulletin 149, U.S. Department of Agriculture, Bureau of Soils.

adapted to the general farm crops, including wheat, corn, oats, barley, rye, flax, and grass.

"The Hagerstown loam is a brown or yellow loam averaging about twelve inches in depth. The subsoil is a yellow or reddish clay loam to a depth of twenty-four inches, but frequently grades into a stiff yellowish-red clay. The type occupies rolling valley land, and is derived from the weathering of pure limestone. This is typical corn soil. It is one of the best general farming types in the Eastern States, and is used for corn, tobacco, wheat, grass, and apples.

"The soil of the Volusia silt loam, to an average depth of eight inches, is a grey to brown silt loam. The subsoil to a depth of two feet is a light yellow silt loam, at which point mottlings of grey or drab are encountered. Both soil and subsoil contain a high percentage of flat fragments of shale and sandstone, ranging from one or two inches to a foot or more wide. In addition, a considerable quantity of finely divided shale fragments is found in both soil and subsoil. The subsoil usually rests at varying depths below eighteen inches on beds of shale or sandstone rock. The type is derived from the weathered products of the shale and sandstone, re-worked by glaciation, and slightly modified by extraneous glacial material. It occupies rolling and hilly land, and is frequently interrupted or bordered by steep slopes not suited to agricultural purposes. The Volusia silt loam where properly cultivated is a good soil for timothy and small grains. In the eastern part of the region where it occurs it lies at too high an elevation to be well adapted to corn. In this region buckwheat and potatoes are grown to advantage."

Each of the above soils was treated with applications of the slag fertiliser, and wheat seedlings were planted. The plants were grown for a period of three weeks, and then weighed and compared with those grown under similar conditions in untreated soil and in soil treated with other forms of potash and phosphatic fertilisers. Since the Volusia silt loam responds readily to treatment with lime, two sets of experiments were run with this soil. In the first no lime was used except that furnished by this slag fertiliser, but in the second set of tests the soil was limed at the rate of two tons to the acre. This was done in order to make sure that any beneficial effect observed from the slag treatment was not entirely due to the basic character of this material.

In Tables VI., VII., VIII., and IX. the results of these experiments are given. The weight of the untreated plants, or checks, is taken at 100, and the weights of the plants grown under similar conditions, but in soils treated with various potash and phosphatic fertilisers, are compared with this figure.

TABLE VI.—*Relative Green Weights of Wheat Plants grown for a period of three weeks in Carrington Silt Loam untreated and treated with various quantities of Potassic and Phosphatic Fertilisers.*

Treatment.	Application per acre.		Relative green weights.	Average.
	K <sub>2</sub> O. Pounds.	P <sub>2</sub> O <sub>5</sub> . Pounds.		
Check .. .. .	—	—	100	100
Slag (33 SB) .. ..	50	60	101	104
Do. .. .. .	100	120	104	
Do. .. .. .	200	240	107	
Potassium sulphate ..	50	—	100	106
Do. .. .. .	100	—	113	
Do. .. .. .	200	—	106	
Acid phosphate .. ..	—	60	101	107
Do. .. .. .	—	120	107	
Do. .. .. .	—	240	114	
Potassium sulphate and acid phosphate ..	50	60	110	109
Do. .. .. .	100	120	110	
Do. .. .. .	200	240	108	

TABLE VII.—*Relative Green Weights of Wheat Plants grown for a period of three weeks in Hagerstown Loam untreated and treated with various quantities of Potassic and Phosphatic Fertilisers.*

Treatment.	Application per acre.		Relative green weights.	Average.
	K <sub>2</sub> O. Pounds.	P <sub>2</sub> O <sub>5</sub> . Pounds.		
Check .. .. .	—	—	100	100
Slag (33 SB) .. ..	50	60	101	105
Do. .. .. .	100	120	107	
Do. .. .. .	200	240	106	
Potassium sulphate ..	50	—	122	127
Do. .. .. .	100	—	129	
Do. .. .. .	200	—	130	
Acid phosphate .. ..	—	60	101	101
Do. .. .. .	—	120	102	
Do. .. .. .	—	240	101	
Potassium sulphate and acid phosphate ..	50	60	111	121
Do. .. .. .	100	120	116	
Do. .. .. .	200	240	136	

TABLE VIII.—*Relative Green Weights of Wheat Plants grown for a period of three weeks in Volusia Silt Loam untreated and treated with various quantities of Potassic and Phosphatic Fertilisers.*

Check .. .. .	—	—	100	100
Slag (33 SB) .. ..	50	60	113	112
Do. .. .. .	100	120	114	
Do. .. .. .	200	240	109	
Potassium sulphate ..	50	—	124	116
Do. .. .. .	100	—	117	
Do. .. .. .	200	—	107	
Acid phosphate .. ..	—	60	109	117
Do. .. .. .	—	120	113	
Do. .. .. .	—	240	128	
Potassium sulphate and acid phosphate ..	50	60	116	115
Do. .. .. .	100	120	119	
Do. .. .. .	200	240	109	

TABLE IX.—*Relative Green Weights of Wheat Plants grown for a period of three weeks in limed Volusia Silt Loam untreated and treated with various quantities of Potassic and Phosphatic Fertilisers.*

Check .. .. .	—	—	100	100
Slag (33 SB) .. ..	50	60	104	116
Do. .. .. .	100	120	110	
Do. .. .. .	200	240	135	
Potassium sulphate ..	50	—	99	114
Do. .. .. .	100	—	142	
Do. .. .. .	200	—	100	
Acid phosphate .. ..	—	60	129	123
Do. .. .. .	—	120	124	
Do. .. .. .	—	240	116	
Potassium sulphate and acid phosphate ..	50	60	110	110
Do. .. .. .	100	120	118	
Do. .. .. .	200	240	103	

Tables VI., VII., VIII., and IX. show that in every case applications of the slag fertiliser to the soils had a stimulating and beneficial effect.

The increase in growth caused by the citric soluble potash and phosphoric acid in the slag was, as a rule, less than that caused by the application of the equivalent quantities of these two fertiliser elements in a water-soluble form, but this is to be expected in the case of experiments carried on for such a short period of time. The tests, of course, are not conclusive, but they indicate that good results may be expected from the use of such a fertiliser.



## Summary.

A method of obtaining both potash and phosphoric acid in citric soluble form has been devised. It consists of mixing together phosphate rock and felspar, with the addition of small quantities of the oxides of iron and manganese to promote fluidity or lower the melting-point of the slag, the mass being then heated to about 1400° C. for about twenty minutes. The resulting product is not only soluble in a 2 per cent citric acid solution, but is also fairly soluble in water saturated with carbon dioxide. Pot tests with typical soils showed that the mineral increased the growth of wheat plants, but the beneficial effect derived from such applications was not on the whole as marked as it was when more soluble forms of phosphate and potash were used. The indications are, however, that the slag product has a distinct high fertiliser value.

## THE COAL-TAR DYE INDUSTRY.\*

THE Special Committee appointed by the New York chemists to investigate and report upon conditions and needs involved in the enlargement of the coal-tar dye industry in the United States reported at the regular stated meeting of the New York Section of the American Chemical Society on November 6th. The meeting had been widely advertised and was unusually well attended.

This Committee was composed of the following members:—J. B. F. Herreshoff, representing the manufacturers of heavy chemicals; I. F. Stone, representing the American coal-tar dye producers; J. Merritt Matthews, representing the textile interests; H. A. Metz, representing the importers; David W. Jayne, representing the producers of crude coal-tar products; Allen Rogers, Chairman of the New York Section; and Bernhard C. Hesse, chemical expert in coal-tar dyes, Chairman.

The findings of this Committee were considered in detail and after discussion the report was unanimously adopted by the Section and ordered to be printed in the *Journal of Industrial and Engineering Chemistry*.

In view of the importance of these recommendations, and the highly representative character of the Committee, their conclusions will doubtless be of the greatest value not only to the chemical profession, but also to the layman interested in our industrial possibilities.

The following is the official text of the report:—

## TO THE NEW YORK SECTION, AMERICAN CHEMICAL SOCIETY.

1. At the meeting on October 9, 1914, the Chairman of this Section was authorised to appoint a Committee to investigate into the feasibility of expanding the chemical and dye-stuff industry in the United States and to report to the Section on November 6, 1914.

2. The undersigned Committee was appointed October 15th, and at once proceeded. It addressed letters of invitation to co-operate to those who have been most active in the public prints in urging the expansion of the chemical and particularly the dye-stuff industry in the United States; further, an invitation was extended to the maker of the motion which resulted in the appointment of this Committee. The assistance from these is nil.

3. A request was addressed to trade publications in the City of New York and to some of the metropolitan dailies; in all, nine such publications were requested to publish a suggested notice for the purpose of inviting co-operation; the object of this Committee was set forth, and request was made that suggestions be mailed to the Chairman of this Committee. All but one of these publications have complied with that request. No help has been obtained

by this Committee from any suggestions mailed to it as a result of this publicity.

4. Your Committee has carefully considered all the public suggestions as to methods of improvement and has searched through the governmental regulations of the belligerent nations as to embargo and as to contraband of war in order to construct therefrom a list of chemicals, inclusive of dyestuffs, which have thereby been shut off from the United States, in the hope of thus being placed in a position to make specific recommendations of value.

5. It can be fairly stated that, in general, the chemical industry of this country is efficiently exploited and is making full use of all the opportunities presented to it under the normal conditions existing prior to the state of hostilities. Some of the chemicals which are imported from abroad are made in considerable amounts in this country as well, and the amounts imported under normal conditions depend upon the ordinary normal fluctuations of business conditions both here and abroad. With the stoppage of this foreign supply the domestic production was not at once capable of making up the deficiency, but in a number of instances the American manufacturers have taken steps to increase their capacity, and the strain in the market of those particular things will exist no longer than it will require to expand the manufacturing facilities to the proper extent.

Among these are:—Ammonia salts, barium chloride, barium nitrate, bleaching powder, sodium cyanide, yellow prussiate, sodium nitrate, sodium hydrosulphite, zinc dust.

6. If, however, it be desired, and if public necessity requires the introduction of the manufacture of explosives and further chemicals and dye-stuffs into our home industry, such as coal-tar product explosives, pharmaceuticals, medicinals and other intermediates, and finished coal-tar dyes, then alterations of our tariff law are inevitable, and the consumers in the first place and the public in general must share in the burden thus imposed. If conditions of national defence in case of attack by a foreign power require us to manufacture our own explosives and to be, in that regard, independent of all foreign nations at all times, or if our textile industries or any other of our industries requiring coal-tar chemicals such as dye-stuffs shall for ever be protected and made independent of foreign nations for the supply of those materials, then the nation as a whole must bear the burden incident to such expansion. Under existing circumstances private enterprise and private capital have gone their limit. They have reached the limit for two reasons:—

I. The explosive, dye, and similar industries abroad, just referred to, are in a state of high development and of refined organisation and are financially the best suited to carry on an offensive campaign against any nation attempting to take business away from them.

II. Domestic manufacturers are prohibited by law from making use of co-operative commercial devices such as pools, trusts, manufacturing and selling agreements and the like, whereas such devices are wholly lawful abroad and are encouraged by the respective governments. In other words, the American chemical industry is expected to cope with the foreign industry while both its own arms are tied behind its back and its opponents have full and free use of their arms.

## Anti-Dumping Clause.

7. The remedies required would include an effective anti-dumping clause that would certainly prevent under-selling of domestic manufacturers in the United States by unfair methods. What the form of such clause should be is a problem with which your Committee is unable to cope; it is strictly a law-making and law-enforcing problem and is allied to the usual problem of determining under-valuation as heretofore carried on by our Treasury Department; it is, however, a much more refined problem than the older problem of proving under-valuation. Nevertheless,

\* Recommendations of the New York Section of the American Chemical Society on the Enlargement of the Coal Tar Chemical Industry in the United States. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 22.

your Committee believes that with such a mechanism in our law, much would be done toward encouraging our chemical industries.

#### *To Create a Coal-tar Chemical Industry.*

8. According to the best information that your Committee can gather, such an anti-dumping clause alone would not be sufficient, however, to create complete and independent domestic coal-tar explosives, dye-stuffs, and medicinals industries. It has been conclusively demonstrated during the past thirty years that the present tariff rate of 30 per cent on dye-stuffs is not sufficient to induce the domestic dye-stuff industry to expand at a rate comparable with the consumption of dye-stuffs in this country, and that therefore all dye-stuffs made from coal-tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal-tar, should all be assessed alike, namely, 30 per cent *ad valorem* plus  $7\frac{1}{2}$  cents per pound specific, and that all manufactured products of or obtainable from coal-tar, themselves not dyes or colours and not medicinal, should be taxed 15 per cent *ad valorem* and  $3\frac{1}{2}$  cents per pound specific.

#### *Tariff to Aid Dye Industry.*

9. The best information and judgment your Committee can obtain is that the above manufactured products of coal tar, not dyes and not colours and not medicinal, should carry one-half the duty of the finished coal-tar dye, and that the above rate of 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents specific would probably be sufficient to encourage and enable domestic manufacturers to expand their operations to such an extent as to supply a very material increase in, if not the whole, of these commodities consumed in this country. The reason for a specific duty is to protect the domestic manufacturer in the manufacture of the relatively cheap dyes such as the cheap scarlets, the cheap yellows and the like, whose prices abroad are in the neighbourhood of from 12 to 20 cents per pound; with dyes of that type 30 per cent *ad valorem* would not offer so serious an obstacle to importation and underselling thereof as does the  $7\frac{1}{2}$  cents per pound specific; on the other hand, on dyes whose prices are 1.00 dols. and upwards per pound the function of the  $7\frac{1}{2}$  cents specific more nearly approaches zero; that is, with the cheap dyes the chief function lies in the specific portion of the duty and with the expensive dyes the chief function lies with the *ad valorem* portion of the duty.

This is said to be the price the nation will have to pay to have a complete self-contained and independent coal-tar chemical industry. However, it must be remembered that if such an industry be created and importation of coal-tar products inclusive of intermediates and dyes is restricted, its ultimate effect upon the Federal revenues will have to be considered. *It will therefore be necessary to determine carefully if the advantages to be gained are equal to the price to be paid.*

#### *Patent Laws.*

10. This Committee is a unit in the belief that an alteration of our patent laws aiming at compulsory working or compulsory licensing would not be of any substantial benefit to this industry or to the country as a whole. Twenty-nine countries have attempted compulsory licensing clauses and fifty-six countries have attempted compulsory working clauses, and the best information your Committee can obtain is that in none of these attempts has there been any appreciable measure of success. While it may be true that under extraordinary conditions, such as now exist, compulsory licensing might have some advantage, yet it is equally true that in normal times the disadvantage due to compulsory licensing or compulsory working would more than overbalance any advantage at all likely to be obtained under stress of unusual conditions.

11. In none of the countries where there have been

working or licensing clauses or both, co-extensive with the existence of the coal-tar chemical industry, has there been established any real coal-tar chemical industry, and your Committee does not feel that an alteration in our present patent laws could be made which would be effective against foreigners and at the same time not be onerous and a hardship to domestic inventors. Your Committee believes that in the long run and in the final outcome, our present system with regard to working and licensing is as efficient as that of any other country. In the dye-stuff industry, in particular, there are so many non-patented commercial products and so many commercial products once patented, now free from patent restraint, that their production alone would form a basis for a very considerable industry, and your Committee feels that the way to encourage that industry, if the establishment of that industry in this country be a national necessity, is through a change in the tariff and the additional anti-dumping feature in the administration of the tariff and not through any change in the patent laws. *Once established, such an industry could develop and ultimately cope with any foreign combination upon fair and equal terms.* Over 90 per cent of the tonnage and of the individual dyes used in the United States will be free from any patent-restraint within the next four years—over 75 per cent of the dyes are now in that condition.

#### *Availability of Raw Materials.*

12. The best information your Committee has so far been able to gather is that this country can produce so-called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry inclusive of explosives and dyes, *provided* there is a certainty of outlet as to volume and continuity. Those engaged in manufacture here do not want to expand unless the dye-users are willing to make corresponding contracts. In other words, it is a closed circle. If the dye-users will contract sufficiently with the dye-makers, the dye-makers will contract with the coal-tar distillers and the industry will take a start. The initiative rests wholly with the users; if they cannot afford to contract, the dye-maker and the distillers cannot afford to make their contracts and additional investments.

#### *Coal-tar Products.*

13. *Benzol, Toluol, and the like* are produced in sufficient amount in present installations of by-product coke-ovens to provide all of these things that would be needed for a coal-tar chemical industry of a magnitude sufficient to supply the United States market; the separation of these materials from the gas that carries them is dependent upon the market and the demand therefor. There is no inherent defect in our coke-industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol, and the like contained in the gas as a fuel than to separate them from the gas and from each other for purposes of sale. Ample supply can be provided before any plant that could use benzol and the like for dye stuff making could be erected in the United States, and thereafter the supply of these materials can readily be kept up to any requirement.

14. The materials of the preceding paragraph are the ones used in the coal-tar explosives industry as well as in the coal-tar medicinals and dye-stuffs industries. Each of these three industries co-operates with the others to make full use of those materials; alone, none can fully make use thereof nor succeed; the correct and proper utilisation of these materials requires successful co-existence of *all three* industries in one and the same country.

15. *Naphthalene and Anthracene* are contained in the tars produced in the United States in an amount sufficient for the needs of a domestic dye-stuff industry and it is merely a question whether it is more profitable to leave them in the creosote oil, where they now occur, or to separate them out of such oil and refine them for purpose

of dye manufacture. Ample supply of either of them could be produced and provided at the same time or shortly after any plant could be erected in the United States for the use of these things in the production of dyes.

16. What has been said with regard to the supplies of naphthalene is also true of the supplies of *creosol*.

17. All the *Creosote Oil* contained in the total amount of coke-oven tar now made is separated from it and used. Increased production of creosote oil requires a greater production of tar, and a greater production of tar is dependent upon increased installation of recovery coke ovens.

18. *Phenol* or *Carbolic Acid* supply is primarily dependent upon our deliberately selected method of coal treatment; to change that treatment so as to get more phenol would entail abandonment of other advantages which would not be compensated for by the increased amount of phenol so produced. Under present circumstances freights and haulages play an important part. At isolated plants, separated by considerable distances from each other, small amounts of phenol are produced, and the separation of the phenol at such individual places would be economically unprofitable, and in order to concentrate this amount of phenol to or at a point where separation could be conducted profitably would entail freight haulages much in excess of the value of the phenol that would thus be transported.

19. The only source of phenol in sight is that produced synthetically from benzol by means of sulphonation and subsequent melting with caustic soda. This depends, in turn, upon our benzol supply and would be profitable only so long as the United States market is not killed by the dumping of foreign phenol thereon, whether such phenol be synthetic or distilled.

20. *Salicylic* production depends upon availability of phenol and the production of *Benzoic Acid* depends upon the availability of toluol which has heretofore been discussed.

21. *Phthalic Acid* made from naphthalene by means of bichromate cannot successfully compete with that made by the mercury and sulphuric acid process which is protected by patents having about three years more to run.

#### Miscellaneous Chemicals and Raw Materials.

22. *Acetic Anhydride* can be made without trouble in this country, and will be made in this country so soon as the domestic demand is large enough and steady enough to warrant the installation of a suitable plant.

23. *Nitric Acid*. All countries with the exception of possibly Norway and the countries importing from Norway, are dependent upon Chili for the raw material for making nitric acid. It will not be profitable to make nitric acid from air in the United States until the value of the electric horse-power reaches a level of 3 or 4 dols. a year, as it is in Norway.

24. *Ammonia* and its salts all depend upon recovery coke-ovens, and such recovery plants are increasing as fast as circumstances will permit.

25. *Barium Chloride* and other compounds of barium may be made from domestic barytes. A number of attempts have hitherto been made, but with indifferent success. Factories established within the last year promise to be successful.

26. *Magnesium Chloride* of a sufficient purity to be used in the production of fluorine is almost generally made from magnesite found in Greece, which is the only deposit known having sufficiently high purity; there are reports of suitable deposits in California and in lower California, so that, with the completion of the Panama Canal, the question of freights, which seems hitherto to have stood in the way of developing these deposits, may be eliminated. Other sources, less remote from centres of consumption, and using other materials, e.g., brine waste, are about to be successfully operated.

27. *Manganese* in the form of pyrolusite is not known to

occur in paying deposits in the United States; these are practically all in the Caucasus.

28. *Potash*.—In view of the great exertions that have been made for a number of years, both on the part of the federal government through a number of its departments and a great many different groups of capitalists, there is nothing to be said in this report that would be of any value with regard to increased production of potash either as fertiliser or as a chemical.

29. *Yellow Prussiate* and *Sodium Cyanide* can be and have been made from domestic materials in such an amount as to provide practically the entire consumption, or a great portion thereof, in this country so long as there was a sufficient duty on them; the present duty is not enough to protect the American manufacturer, and those who were engaged therein have in large measure withdrawn from the business, but some are reported to be taking up manufacture cautiously and in limited amounts.

30. *Hydrosulphites* in solution can be made from domestic materials without interference with any patent rights; the production of solid salts and derivatives are, however, still protected by patents that have a few years more to run.

31. *Sodium Nitrite* is produced more cheaply as a by-product in Norway than it can be produced anywhere in the world; unless the price of the electric horse-power in this country sinks to a 3 or 4 dols. level per year, as in Norway, this product cannot be manufactured in the United States.

32. *Oxalic Acid* is and has been made to some extent in this country and the information coming to your Committee is that suitable efforts are being made to expand the capacity of existing plants.

33. *Tartaric Acid* and *Citric Acid*.—To make this country independent of others, with respect to tartaric acid and citric acid would call for radical changes on the part of our grape growers and our lemon growers as to the policy of their business.

It is probably true that edible grapes do not produce argols (the crude material for tartaric acid) very largely, and that our domestic lemons do not produce as large yields of juice (the crude material for citric acid) nor as high an acidity as do the Italian lemons; therefore an independent supply of the raw materials produced in the United States for tartaric and citric acids is, in the first instance, an agricultural problem, and in the second instance a market problem.

#### General Remarks.

34. Finally, it should be pointed out that the United States is by no means the only country whose chemical and allied business has been strained or upset by the European war. Each and every other country has felt the strain. British committees have gone into this same subject of expanding British chemical industries, and, not only that, but also into the question of making their very basic necessities, and the reports have so far been adverse to any immediate relief by domestic manufacture. The Boston Chamber of Commerce, through its Committees, has arrived at the same conclusions for this country.

35. It is further clear that the stability of a complete domestic chemical industry, in so far as it depends upon foreign supplies, is bound up to a successful merchant marine and to an efficient foreign banking condition just as is all our foreign business.

#### Findings.

36. Your Committee finds as follows, as to the facts:—  
I. Prior to the hostilities, domestic chemical industry was utilising and exploiting every reasonable opportunity to its full extent.

II. Since the outbreak of hostilities, domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome.

III. Since the outbreak of hostilities, domestic plants that had heretofore been shut down or partly dismantled

because of disastrous foreign competition are said to have resumed operation with caution.

IV. That a 30 per cent duty on some coal-tar dyes for over thirty years has not produced a real coal-tar dye industry in this country.

#### Conclusions.

37. Your Committee submits its conclusions as follows:

A. To prevent the unfair underselling alleged to be practised by foreigners in this country, the adoption of an effective anti-dumping clause.

B. The so-called coal-tar "intermediates" which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinals, and dye-stuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes; all coal-tar dyes *without exception* should be taxed alike, namely, 30 per cent *ad valorem*, and 7½ cents per pound specific.

C. Changes in the patent laws, such as by compulsory licensing or compulsory working clauses, are *wholly ineffective, do more harm than good, and should not be attempted.*

Your Committee recommends that this Report be submitted to the appropriate Committees of Congress. Further, that this Report be forwarded to interested organisations.

BERNARD C. HESSE, Chairman.  
J. B. F. HERRSHOFF.  
I. F. STONE.  
J. MERRITT MATTHEWS.  
H. A. METS.  
D. W. JAYNE.  
ALLEN ROGERS.

#### THE WAR EXHIBITION, 1915. INTERESTING EVENT IN AID OF THE BELGIAN RED CROSS.

IN view of our incalculable indebtedness to the gallant Belgian nation, a War Exhibition has been organised to assist the Funds of the Belgian Red Cross Anglo Belgian Committee, whose Patroness is H.M. the Queen of the Belgians.

The War Exhibition, 1915, is designed to present in an interesting and instructive manner an idea of the extent to which science and industry are being utilised in every branch of the present gigantic struggle.

A striking feature is a magnificent 13,700 sq. ft. mural panoramic representation of Belgium. This portrays amongst other scenes the beauties of Brussels, Antwerp and its magnificent port, Bruges (the Venice of the North) with its many bridges, Ghent, Ostend and the coast, Liège, Namur, and the Valley of the Meuse, including the ill-fated Dinant, Louvain, Malines, Ypres, and Visé, the first town to fall temporarily under the iron heel of the barbaric Hun.

As the War Exhibition, 1915, will be the only important exhibition in London throughout the coming summer, it should prove a great stimulus to recruiting.

The exhibition is to be made as comprehensive as possible in the space at disposal, and the leading representatives of the Allied and Neutral Governments will be specially invited to visit and interest themselves in the exhibition, so that the event may afford a unique opportunity for manufacturers and business houses to bring forward their products, and thus help in the solution of the problems of equipment, food, hygiene, &c., each of which plays so important a part.

The Prince's Skating Club, Knightsbridge, S.W., situated in the best part of London, has been selected as the most suitable place in which to hold this exhibition. A continuous service of motor buses and tube trains provides the easiest and quickest of access from all parts of the

Metropolis, as it is within a few minutes' walk of Knightsbridge Station and Hyde Park Corner, and other stations whence connection is made with all London termini.

Offers of interesting war trophies as loan exhibits, or assistance of every kind towards making the exhibition the great success it deserves to be on account of its object, will be welcomed by the Hon. Organising Secretary, War Exhibition, London Chamber of Commerce, 97, Cannon Street, London, E.C.

#### WELSH NOTES.

(By Our Special Correspondent).

THE trade of Swansea Port last week displayed considerable activity, and the figures exceeded last year's average. Among the imports were included 775 tons of steel scrap from France, 2400 tons pig-iron from Spain, 5200 tons brimstone from Italy, 3100 tons iron ore from Algeria, and 4077 tons copper regulus, 44 tons precipitate, and 19 tons of copper from Cape of Good Hope. Patent fuel work was very brisk in all the Welsh ports, 16,985 tons being exported from Swansea and 7303 tons from Port Talbot. Tinplates were also plentiful in Swansea—77,483 boxes being shipped, whilst 88,337 boxes were received from the works. Stocks in the dock warehouses and vans totalled 331,335 boxes, compared with 320,481 boxes the corresponding week of last year.

Taking the chemical and allied industries throughout the Swansea Valley there was a decline in some trades as compared with the previous week, which was most marked in the tinplate industry. There was an increase in the production of pig-iron, much pressure being observed at the blast furnaces. All steel-works were very busy, and employment was generally good, partly on account of Government work. Steel bars found a large demand for home consignments, and the aggregate production of copper was heavy, but in some quarters a scarcity of labour was noticeable. Employment was slack in most of the departments of the tinplate industry, and it was only fair at the sheet mills, with the exception of Pentardawe, where five sheet mills were put into operation. Two tinplate mills were also re-started at the Upper Forest, Morriston, following the settlement of a minor dispute. The tinplate trade showed little sign of revival at Port Talbot, where it has been at low ebb for some considerable time. The spelter trade was very brisk, and Government orders accounted for much of the work. The safety fuse and lead pipe works have also had a busy week, whilst the Mannesman Tube Works and the Mond Nickel Works compared favourably with previous weeks. The iron and brass foundries did good work, and there was an improvement in the moulding and smelting furnaces. Sulphuric acid factories showed few signs of enlivenment, the demand for vitriol being very small, but the chemical manure works were very brisk.

Dowlais Steel Works had a very busy week; the blast furnaces, the Bessemer, and Siemens being particularly busy, the supply of molten metal to the converters being well maintained. The Goat Mill turned out heavy steel rails, steel sleepers, cogging steel, and bars; the Big Mill being engaged in sole plates, fish plates, fritters, props, and tram rails. There were a couple of idle days over the holidays at the mills, when some minor repairs were seen to.

Society of Chemical Industry.—The next meeting of the Section will be held at the Chemical Society's Rooms, Burlington House, Piccadilly, on Monday, June 7, at 8 p.m. Mr. J. W. Hinchley will move that certain alterations be made in Rule 9 of the Section By-laws.

## PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

Ordinary Meeting, May 14, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER, entitled "*Precision Resistance Measurements with Simple Apparatus*," was read by Mr. E. H. RAYNER.

The paper describes methods by which the comparison of resistances can be made to an accuracy of 1 in 10,000 or higher by using simple apparatus usually available in electrical laboratories, or which can be easily constructed with little skilled assistance.

The comparison of nominally equal resistances of 1 ohm and upwards by the usual method of shunting one side of a nearly balanced quadrilateral by a high resistance is mentioned, and variations on this when only part of one resistance is shunted are often useful. The great advantages of having resistances capable of carrying comparatively large currents is illustrated, especially for measuring changes of resistance of commercial apparatus under working conditions. The determination of errors in a volt box for use with a potentiometer is described at some length. This is of especial importance in precision photometry.

If a sufficient continuous-current voltage is not available for testing such apparatus as high-potential dividers, it is shown that using sufficient continuous current to secure sensitivity the heating may be supplied by superposed alternating current.

Resistances in common use are very generally of simple numerical value, and a Kelvin bridge specially designed for the comparison of such resistances is described. It consists essentially of two rows of 25 resistances of 20 ohms each.

## DISCUSSION.

Colonel SQUIER thought the paper was very useful and likely to be generally helpful.

Mr. F. E. SMITH thought the paper would prove of considerable service to many who were faced with the problem of measuring accurately resistances of indiscriminate types. He might take exception to the lettering of the diagrams. Ever since 1861 all bridges had been lettered P, Q, R, and S. The custom was practically universal, and it was advantageous to follow it in all cases. The author stated that when the current in a bridge is reversed the potential of the galvanometer is suddenly altered. This was not so in the case of equal ratio arms. Again, it was stated under Fig. 1 that A and B, when not equal to P and Q, should be in series as regards the supply current to obtain maximum sensitiveness. He worked out on the board a case in which this did not hold. The method of substitution, while of extreme usefulness, was not always the best to employ in a given case, and he showed an arrangement for use with a resistance with potential leads which was simpler and more convenient in practice. With regard to the measurement of incommensurable resistances, he pointed out that in the type of bridge used for resistance thermometry we had ready to hand all that was necessary for the determination of any resistance from a very low to quite a high value with great accuracy. Moreover, the bridge could be calibrated with ease, which was a considerable advantage.

Mr. DUDDELL said that with regard to the building up of resistances he had in his laboratory a large number of 2000  $\omega$  coils which were capable of carrying 0.1 ampere. By arranging these units in series and parallel combinations he could readily obtain any ratio he wished, and the building up of a potentiometer with these coils was very easy and convenient. An advantage in the use of high resistance coils such as 2000  $\omega$  for work of this kind was the relative unimportance of the connection errors, which were very small if the resistances had substantial plug contacts.

Mr. A. CAMPBELL said that he had introduced the system of non-inductive winding on channelled frames about sixteen years ago, and it had been publicly in use in the National Physical Laboratory for many years. It appeared to have been patented recently by a foreign firm. The lessening of the inductance is obtained by winding a left and right-handed coil in the same set of channels and connecting them in series, tying the contiguous pairs of wires closely together. The capacity is well distributed if many channels are used. In a simpler method, which he has also used for many years, a single wire is twisted into a large number of loops, in each of which the wires are very close together, and each channel carries a single loop.

Mr. C. C. PATERSON said that it was inevitable when working with ordinary resistances on a high voltage that a good deal of heat should be dissipated. In potential dividers one makes the coils all of the same wire, measures the ratios at low currents and relies on these remaining the same at high currents. This is not the case, however, the ratio altering by an appreciable amount depending on the precise position of the portion from which the voltage is picked off—e.g., at the end or the middle of the coils—on account of unequal temperature distribution. He instanced a case in which errors of two or three parts in 10,000 were introduced from this cause, and said that the method of superposing an alternating voltage on a small direct-current voltage was very useful for determining the ratios under the working conditions of heat dissipation.

Mr. D. OWEN was surprised to observe that the author claimed to measure a resistance to 1 or 2 parts in 10 million. With coils of platinum-silver a change of temperature of 1° C. would change the resistance by about 260 parts in a million, yet no temperatures were stated in the examples quoted, nor was any reference made in the first method to the heating effect of the current in the various resistances. He thought that the paper, therefore, gave a wrong impression of the precision which was possible in such measurements. In the method to which Fig. 2 applies the author requires four measurements to eliminate the resistance of the connecting piece. Could this not be much simplified by connecting the galvanometer to the middle of L, thereby reducing the measurements to two? As regards the 2.6 law connecting R and C, he failed to see how it was possible to neglect, as the author had done, the heating of the three-in-series three-in-parallel group. Each component of that group would carry one-third as much current as the single resistance, and would, therefore, have one-ninth as much heat dissipated in it. The neglect of this might account for the departure from the square law.

Dr. C. V. DRYSDALE, in a communication which was read by the Chairman, said he was surprised that the author had adopted the method of shunting in place of the more convenient slide wire. In 1907 he had combined the principles of the Carey Foster and Kelvin bridges in a bridge which was simple to construct and susceptible of the highest accuracy. When the resistances compared are nearly equal their difference is given directly in millionths of their value. By means of a self-contained ratio bobbin it is possible to step up or down so as to obtain most of the uneven ratios which are required. The bridge forms an accurate series of standards built up from a single unit, and is, moreover, self checking. In Mr. Rayner's bridge contact errors in connecting his ratios do not seem to be eliminated, and it is not self checking. He was pleased to see that the author realised that contact errors can be minimised without great loss of sensitiveness by keeping the resistance of the ratio coils moderately high. In practice these need never be reduced below 10 or even 100 ohms.

Mr. RAYNER, in reply, said that it seemed easier in discussing bridges to use such letters as A B for the resistances to be compared and other letters well separated from them in the alphabet for the secondary resistances. He had often been troubled in following the discussion of



methods by the difficulty of keeping in mind these differences when P, Q, R, S are used. Any criticisms by Mr. Smith concerning arrangement of the resistances in the quadrilateral as regards the current supply were welcome. He agreed with Mr. Duddell as to the size of unit to be used when a number of resistances are to be used in series and parallel. They should not be less than 1000 ohms, unless errors are very carefully guarded against. He agreed with Mr. Owen that a sensitiveness to such a figure as, say, 1 in 10,000,000, does not necessarily imply similar accuracy of measurement, and the proof of the full use of the sensitivity lies in reproducing the numerical value on repeating the measurement. All the examples given have been reproducible in this sense. This does not mean that identically the same shunting resistances have been required on repeating a series of measurements, as very small temperature changes in a few minutes will affect the result; but it does mean that if, for instance, on repeating a given experiment, a different shunting resistance is required in the one position, an exactly equivalent change is found in the other position, showing that the measurement takes full advantage of the sensitivity available. The suggestion of connecting the galvanometer to the middle of L in Fig. 2 is impracticable by reason of the resistance of the end contacts. He did not think he should call Dr. Drysdale's methods "simple" and available with apparatus ordinarily to be found in any laboratory or easily constructed with little skilled assistance. The other points he mentioned must wait till he could examine them in detail.

A paper, entitled "*Some Novel Laboratory Experiments*," was read by G. F. W. JORDAN, A.R.C.S., B.Sc.

*Condensation Calorimeters for the Measurement of Latent and Specific Heats.*—(a) It is shown how an ordinary vacuum jacket flask can be converted into a suitable condensation calorimeter. Errors arising from loss of heat and wetness of the vapour are almost eliminated by making two experiments; (b) another condensation calorimeter is constructed on a different plan with a view to the elimination of the same errors.

*The Thermal Conductivity of a Narrow Metal Bar.*—Gray's apparatus for the measurement of the conductivity of a narrow bar has been modified for the purpose of rendering the loss of heat relatively small and reducing the time taken in the measurement, thus introducing the experiment to the elementary student.

*The Measurement of Poisson's Ratio for a Rectangular Lath.*—Two mirrors are attached to opposite sides of the bent lath for the measurement of the anti-elastic radius of curvature, and Poisson's ratio is then deduced from the observations in the usual manner.

*A Method of Measuring the Coincidence Period of a Kater and a Clock Pendulum.*—The kater and the clock pendulums are electrically connected so that when at the centres of their swings a momentary current passes through a telephone receiver.

*A Differential Telephone Receiver.*—An ordinary receiver is connected to the secondary of a simple differentially wound transformer, and it is thus converted into a differential receiver for the purpose of electrical measurement.

*Experiment on Interference Fringes.*—The fringes produced by a Lloyd's mirror in white light are nearly achromatized by a simple grating on smoked glass. Other suggestive interference effects with the grating are also described.

#### DISCUSSION.

Mr. F. E. SMITH asked why in the thermal conductivity experiment four rods were used instead of one of four times the cross-section?

Mr. H. MOORE admired the ingenuity of the pendulum experiment, but thought that to make an experiment too simple and free from corrections made it much less instructive to students. He thought the eye and ear method of observing coincidences was one in which students should be trained as much as possible.

Mr. JORDAN, in reply to Mr. F. E. SMITH, said that the use of four thin rods rather than one thick one was advisable, as there was a smaller temperature drop between the end of the rod and the calorimeter when the former was thin than when it was thick.

A paper "*On Electrically Maintained Vibrations*," by Mr. S. BUTTERWORTH, M.Sc., was taken as read in the absence of the author.

#### CHEMICAL SOCIETY.

Ordinary Meeting, May 6, 1915.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Messrs. Richard Berncastle and Robert John Caldwell.

The PRESIDENT, referring to the Memorial presented by the Society to the Government, announced that the united deputations of the Royal Society and the Chemical Society had been received by the Presidents of the Boards of Trade and Education on May 6.

Certificates were read for the first time in favour of Messrs. Pinzen Cheng, F.Sc., 68, Loudoun Road, St. John's Wood, N.W., and Frank Peachey, B.Sc., Woodbridge, Suffolk.

Messrs. H. E. Watt and C. S. Ellis were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected:—Frank Theodore Alpe; Alfred Louis Bacharach, B.A.; Frederick Charles Ball; John Lloyd Bentley; Premananda Das, M.Sc.; Reginald Ernest Essery, B.Sc.; Henry Jackson Evans, B.Sc.; Robert Edward Forbester, M.Sc.; Harri Heap, M.Sc.; Charles Hinde; Nikolai Semenovitch Kurnakov; Colin Henry Lumsden, B.Sc.; John Ernest Mason, B.Sc.; Thomas Dagomet Morson; Henry Taylor Fowkes Rhodes; David Charles Roberts; Leonard Richmond Wheeler, B.Sc.

The following papers were read:—

"*The Rotatory Dispersive Power of Organic Compounds. Part VI. Complex Rotatory Dispersion in Ethyl Tartrate.*" By THOMAS MARTIN LOWRY and THOMAS WILLIAM DICKSON. Part VII. "*Complex Rotatory Dispersion in Methyl Tartrate.*" By THOMAS MARTIN LOWRY and HAROLD HELLING ABRAM.

"*The Formation of Chlorinated Bases from Nitro-compounds on Reduction.*" By WINIFRED GRACE HURST and JOCELYN FIELD THORPE.

Ordinary Meeting, May 20th, 1915.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Mr. John Walter Smith.

Messrs. C. H. Lumsden, H. J. Evans, and R. E. Essery were formally admitted Fellows of the Chemical Society.

A certificate was read for the first time in favour of Mr. William Alfred Bromwich, 4, Lambeth Palace Road, S.E.

A certificate has been authorised by the Council for presentation to ballot under By-law 1. (3) in favour of Frederick Louis Armitage, Albert Road, Devonport, Auckland, New Zealand.

The following papers were read:—

"*A New Method of Estimating Bromine and Chlorine in Organic Compounds.*" By PHILIP WILFRED ROBERTSON.

"*Studies on the Walden Inversion. Part II. The Kinetics and Dissociation Constant of Phenylchloroacetic Acid.*" By GEORGE SENTER.

"*The Constituents of Gloriosa superba.*" By HUBERT WILLIAM BENTLEY CLEWER, STANLEY JOSEPH GREEN, and FRANK TUTIN.

## OBITUARY.

DR. HUGO MÜLLER, F.R.S., Ph.D., D.Sc.

We regret to have to announce that Dr. Hugo Müller, a Past-President of the Chemical Society and until recently the Treasurer of the Lawes Agricultural Trust Committee, died on May 23 at the age of eighty-one. Dr. Müller was an active worker and an able experimenter in organic chemistry, and was the author of many articles and papers upon the chemical constituents of various plants, such as cocositol, quercitol, &c. He was also a keen botanist, and had a wide knowledge of horticulture. He investigated the action of nitrous acid upon naphthylamine, and of nitric acid upon the hydrocarbons of the benzene series, and published papers upon the preparation of carbon tetrachloride and of chrysammic acid, the composition of carmine and creosote, hydrocyanrosaniline, and phenylphosphoric acid. He was the author of a book entitled "Vegetable Fibre and its Preparation for Industrial Uses." For many years he was a partner in the firm of De la Rue, but left the firm in 1902, and since his retirement had worked at the Davy-Faraday Laboratory of the Royal Institution. Dr. Müller was elected a Fellow of the Royal Society in 1866, and served on the Council from 1883-85, and again from 1889-91.

## CORRESPONDENCE.

## WATER CLARIFICATION.

To the Editor of the Chemical News.

SIR,—I should be glad to know from one of your readers what to do in the following case:—

I have bored for water through chalk and found it at a depth of 125 feet, but it contains so much iron that it is not fit for drinking, and until the iron has been allowed to settle it is not of much use for washing purposes. Is there any means of precipitating the iron, or better still of filtering the water? I have been put to very great expense, but would not mind a little more for the sake of getting pure water.—I am, &c.,

C. B. NEATE.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Bulletin de la Société Chimique de France.*  
Vol. xvii.-xviii., No. 3, 1915.

Catalytic Hydrogenation of Liquids under the Influence of Common Metals at Moderate Temperatures and Pressures.—André Brochet, Maurice Bauer, and André Cabaret.—The two first authors have shown that in presence of nickel aliphatic compounds with ethylenic bonds can very readily be hydrogenated under pressures of some kilograms per centimetre. Thus free cinnamic acid or its compounds are particularly easily hydrogenated. The reaction can also be effected under atmospheric pressure, and though, generally speaking, it is slower, the operation is often very useful practically, especially as there is no need of special apparatus. The reaction is rather capricious, for with some substances it proceeds very readily and much more slowly with others, for no apparent reason. With essence of mustard no hydrogen whatever could be fixed.

## MISCELLANEOUS.

**Research Scholarships in Technology.**—It is announced that not more than ten Research Scholarships in Technology (one of the value of £80, three of the value of £75, and six of the value of £50, all with fees remitted) will be awarded on or about July 5, 1915. These scholarships are tenable during the academic year 1915-16 in the Manchester School of Technology (Faculty of Technology in the University of Manchester). Applications must be received on or before June 21, 1915. Forms of application and all information may be obtained, by letter only, addressed to the Registrar, School of Technology, Manchester. Research may be undertaken in any of the following departments:—Mechanical Engineering; Electrical Engineering; Sanitary Engineering. Applied Chemistry: (a) General Chemical Technology; (b) Chemistry of Textiles (Bleaching, Dyeing, Printing, and Finishing); (c) Paper Manufacture; (d) Metallurgy and Assaying; (e) Chemical Technology of Brewing; (f) Electro Chemistry; (g) Photography. Textile Industries. **Regulations.** 1. The appointments will be made by the Governing Body on the recommendation of the Board of Studies, based on the consideration of documentary or other evidence furnished to the board. 2. The scholarships are open to graduates of any university in the British Empire, and to other persons possessing special qualifications for research. 3. The Head of the Department concerned will be required to furnish quarterly to the Board of Studies a short report as to the progress of the research, and at the expiration of the tenure of the scholarship the holder will be required to make a report to the Board of Studies, setting out the course pursued and the results obtained, such report to be typed on foolscap paper and three copies furnished, unless the Board of Studies determines otherwise in any particular case. 4. The research scholar will work under the direction of the professor or lecturer in the subject concerned, and must pursue his research in the School of Technology in accordance with a scheme of study approved by the Board of Studies in the beginning of the academic year, and he will be expected to devote the whole of his time to the prosecution of the research upon which he is engaged. 5. The Governing Body reserve the right of publishing, in such form as they may think fit, the results of researches completed by scholarship holders. 6. The scholarships may be renewed for a second year on the recommendation of the Board of Studies. Extract from the ordinances of the Faculty of Technology of the University of Manchester:—"The degree of Master of Technical Science (M.Sc.Tech.) may be conferred on—(a) Graduates (or persons who have passed the final examination for a degree) of approved universities who, without having taken previously a lower degree of this university, can give sufficient evidence of their qualifications, and have conducted research work approved by the Faculty during a period of two years in the university."

## MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Royal Institution, 3. "Methods of Presenting Character in Biography and Fiction" by W. Ward.  
— Royal Institution, 5. General Meeting.  
— Society of Chemical Industry, 8. "New Process for the Refining of Chile Saltpetre," by J. B. Hobbs.  
— "Method of Testing Mineral Lubricating Oils for Use in Forced Lubricating Systems for Steam Turbines," by A. Philip.  
— "Application of Adobe as a Material for the Construction of Buildings for the Manufacture and Storing of Explosives," by Major Ferris.
- TUESDAY, 8th.—Royal Institution, 3. "The Evolution of Steel—Influence on Civilisation," by Prof. J. O. Arnold, F.R.S.
- THURSDAY, 10th.—Royal Institution, 3. "Method of Presenting Character in Biography and Fiction" by W. Ward.
- FRIDAY, 11th.—Royal Institution, 9. "Music and Poetry," by Dr. H. W. Davies.
- SATURDAY, 12th.—Royal Institution, 3. "Mary Queen of Scots," by Prof. R. S. Rait.  
— Biochemical Society. (At the Rothamsted Experimental Station, Harpenden, Herts.).

# THE CHEMICAL NEWS.

VOL. CXI., No. 2898.

## THE CHEMICAL INDUSTRIES OF GERMANY.\*

By Prof. PERCY F. FRANKLAND, F.R.S.

(Continued from p. 268).

**Explosives.**—I have already mentioned the importance of nitrates and of nitric acid, and have referred to the employment of the greater part in agriculture; of the remainder the major part goes in the manufacture of explosives and in the coal-tar colour industry.

Black powder, or gunpowder, is said to have been discovered by the English monk, Roger Bacon (1214—1294). Gun-cotton was discovered by Schonbein in Basle and Christian Bottger in Frankfurt in 1846.

Nitroglycerin was discovered by Sobrero in Pelouze's laboratory in Paris in 1847, and first manufactured on a large scale as an explosive by the Swede, Alfred Nobel, in 1862.

The disruptive properties of gun-cotton are greatly moderated by gelatinising by means of solvents (acetone, acetic ester, alcohol, and ether, &c.), and by mixing with nitroglycerin ballistic materials like cordite and other smokeless powders are obtained. There is another class of explosives which combine great safety in handling with enormous disruptive effect. Picric acid (discovered by Woulfe of London in 1771), but first used by the French under the name of melinite for filling shells in 1881, and later by the English under the name of lyddite. More recently this has been replaced by trinitrotoluene, first proposed by Haeussermann in 1891 for filling shells, and used by our service under the mark "T.N.T." It is even less sensitive to shock than picric acid. "Ammonal," used by the Austrians for shell-filling, is a mixture of T.N.T. with ammonium nitrate, charcoal, and aluminium powder. It is both very safe and very powerful. T.N.T. is much used for demolishing bridges. It is so insensitive to shock that it is not exploded on being struck by a rifle-bullet, and when in a shell it withstands the impact of the latter piercing an armour-plate (Macnab, "Explosives," Inst. of Chem. Lecture, 1914).

Tetra-nitro-aniline, obtained by Flürscheim, enjoys the unique position among explosives of having been discovered in this country. It is said to be equally safe and even more powerful than trinitrotoluene.

According to the late Oscar Guttman the production of nitroglycerin explosives in 1909 was as follows:—United States, 20,000; Germany, 10,300; England, 8100; Transvaal, 8000; Canada, 5000; Spain and Portugal, 3500; Austria-Hungary 2300; France, 1500 tons; Switzerland, Australia, Norway, and Sweden, 600 tons each; Russia, Italy, Holland, Belgium, 500 tons each; Greece, 175 tons.

Explosives are of enormous importance also in civil life. In mining and engineering modern explosives have greatly accelerated progress and have rendered possible such works as the Panama Canal. They are also being now employed with great advantage in afforestation for loosening the ground in which trees are to be planted. The manufacture of explosives in Germany is very highly developed. The total German production of 40,000,000 kilogrms. includes dynamite explosives, 10,000,000; ammonium nitrate explosives, 16,000,000; and black powder, &c., 14,000,000 kilogrms. There were exported in 1908 value about £1,000,000, and in 1912 £3,000,000.

The world-production of explosives is now about 400,000,000 kilogrms., or ten times the German total

output. We have at Ardeer, in Scotland, the largest explosives factory (Nobel's) in the world, covering 850 acres, employing 1800 men and 700 women, and producing annually about 16,000 tons of all kinds of high explosives.

**Artificial Silk.**—An eminently peaceful industry which is closely related to that of explosives is the production of artificial silk and celluloid. The manufacture of artificial silk has grown up during the past twenty-five years, for this product was first shown by Count Hilaire de Chardonnet at the Paris Exhibition of 1889; he discovered the method of its preparation whilst a student in the Ecole Polytechnique at Paris, and in 1891 formed a company at Besançon, with a capital of £240,000, for its manufacture.

The chief kinds of artificial silk are:—(1) Nitrated cellulose (soluble in alcohol-ether) silk (denitrated by ammonium sulphide) (Chardonnet silk). (2) Ammonio-cupric oxide cellulose silk (Pauly, Fremery, or Urban silk, of the Vereinigte Glanzstoffabrik, Elberfeld, 1897). (3) Viscose silk (CS<sub>2</sub> in presence of NaOH or Ca (OH)<sub>2</sub> on cellulose) (Cross and Bevan). (4) Acetate silk (acetic acid on cellulose) (Cross and Bevan).

Germany produces about 2,000,000 kilogrms., value about £1,200,000, exports 600,000 kilogrms., and imports 1,800,000 kilogrms.; the imported is principally "alcohol silk," due to disadvantageous alcohol tax in Germany. Germany is the principal user of artificial silk, although the fundamental discoveries upon which the manufacture is based are largely due to French and English chemists. The world production is estimated at about 7,000,000 kilogrms.

The distribution of the industry may be gathered from the following:—France, 7 factories; Germany, 8; Belgium, 3; England, 2; Spain, 1; Austria Hungary, 4; Russia, 3; America, 3; Japan, 1.

Great profits have been made out of artificial silk (some of the companies have paid 50—100 per cent dividends), and the price has greatly fallen since its introduction from 28s. to 32s. per kilogr. in 1903, 16s. in 1906, and 12s. (poorer qualities 6s. to 8s.) in 1910.

The cellulose industries furnish a particularly striking example of the manner in which chemical research and invention are able to enhance the value of the kindly gifts of the earth. Thus, one cubic metre of wood has value as fuel about 6s.; (after boiling with lime, soda, and sulphite) as paper pulp, £1 12s.; ditto as paper, £2 16s.; pulp converted into artificial silk, £80 to £240.

**Industries dependent on Synthetic Organic Chemistry.**—It is out of the profound study of synthetic organic chemistry which has been made during the past sixty years that the industries of artificial dyes, drugs, and perfumes have incidentally arisen. The earlier and pioneering achievements in synthetic organic chemistry are well distributed amongst the nations of Europe. (England and France were, however, more especially to the fore). But during the major part of the sixty years the great bulk of the discoveries in this domain have been made in Germany. Organic chemistry is, perhaps, the branch of science which more perfectly suits the German mind and temperament. It involves the possession of those qualities in which Germans are so pre-eminent—the capacity for taking an infinitude of pains, the capacity to anticipate difficulties and organise means to circumvent them. It is, moreover, only possible to make substantial advances in the problems of organic synthesis if the master has at his disposition a number of highly qualified and docile assistants and apprentices; in a word, the master must be at the head of a large and efficient school of research. It is in the possession of such schools of research, both in the universities and in the chemical factories, that Germany has by two generations the lead of all other countries in the world. Whilst most of the professors of chemistry in our own universities and colleges have under great difficulties and without any sort of encouragement been more or less successful in building up such schools of research,

\* Meeting held at Birmingham University on March 4, 1915. From the *Journal of the Society of Chemical Industry*, xxiv., No. 7.

which are, however, by no means slavish imitations of the German model, the chemical manufacturers of this country have, with some notable exceptions, failed to establish anything worthy of the name of research laboratories in connection with their works.

It is in respect of the works research laboratory that there is the greatest contrast between the chemical industries of Germany and those of other countries, and it is not surprising, therefore, that the present war should have served to emphasise the class of chemical products for which we are almost entirely dependent on Germany. (Only about one-tenth of the annual value of dye-stuffs consumed in England is produced in our own country). It is precisely those products—artificial dye-stuffs, artificial drugs, and artificial perfumes—which are the outcome of the works research laboratories, that are now in many cases unobtainable in consequence of the cutting off of the German sources.

The seriousness of the situation is apparent from the following figures, relating to dye-stuffs alone:—The value of dye-stuffs consumed in England annually is £2,000,000, and the value of trade in which these dye-stuffs are employed is £200,000,000, whilst upwards of 1½ million workmen are dependent upon these industries. The total value of dye-stuffs imported into the United Kingdom in 1913 was £1,892,055, of which Germany contributed £1,730,821.

Perhaps the most concise way of conveying a superficial idea of these industrial products of organic synthesis will be by means of the following classification:—

**I. Artificial Products.**—Colours first obtained from aniline by Runge in 1834, by the action of bleaching powder. Aniline colours: Mauve was discovered by Perkin in 1856, and magenta by Verguin in 1859. Azo colours were discovered by Griess in 1859, and introduced on an extended scale in 1878. (Both azo and eosin colours were kept as secret products, but the colours were investigated by Hofmann and their mode of production published, to the great consternation of the inventors). The azo colours have achieved an enormous importance, and have practically banished cochineal and logwood from the dye works. Some 2000 azo colours are now in use. Congo colours, substantive cotton dyes, were discovered by C. Böttiger in 1884.

It must not be supposed that British colour manufacturers have been idle from the days of Perkin; thus, in 1880 a very original departure was made by Messrs. Read, Holliday, and Sons, who introduced the principle of developing azo dye-stuffs on the fibre with their so-called ingrain or ice colours. Some of these have achieved a great success; thus, 2000 tons of *p* nitraniline are now annually manufactured for the production of nitraniline-red and similar colours (G. T. Morgan, "Modern Dyes and Dyeing," Royal Dublin Society, 1914; Cain and J. F. Thorpe, "The Synthetic Dye-stuffs and Intermediate Products," 1913). Again, the discovery of primulin and the colours which can be derived from it by A. G. Green, in 1887, is another very notable achievement. Eosin colours were discovered by Caro in 1873.

**II. Artificially produced Natural Products.**—This group contains substances occurring in nature and long valued by man. The chemical nature of these substances has been carefully ascertained by chemists, who have then deliberately set to work to devise methods for their artificial preparation at such a cost as to compete with and ultimately supplant the natural product. These campaigns against the commerce in the products of nature undoubtedly constitute one of the most remarkable phenomena in the history of the world. Bear in mind, it is the production and supply to man of the actual products of nature, but more cheaply than they can be produced and supplied by Nature herself. These endeavours have already been successful on a very large scale.

**Alizarin** (the essential principle of the madder root) was first synthesised by Graebe and Liebermann in 1869. At

the time of this discovery the world production of madder was 50,000,000 kilograms., roots (1—1½ per cent alizarin), representing ½—¾ million kilograms. alizarin, value £2,250,000. In 1870 France had 20,000 hectares (50,000 acres) under madder cultivation, which soon disappeared after the introduction of the artificial product.

The production of artificial alizarin was:—1873, 100,000; 1877, 750,000; 1884, 1,350,000; 1900, 2,000,000 kilograms. (four-fifths of this was produced in Germany).

A great number of most valuable artificial dye-stuffs, more or less closely related to alizarin but not occurring in nature, have been prepared by chemists, and the total value of the alizarin-colour exports of Germany at the present time is about £1,000,000.

**Indigo.**—This most highly prized blue dye-stuff of both the ancient and the modern world was first artificially synthesised by Adolf Baeyer in 1880, but it required seventeen further years of unremitting and laborious investigation in the works of the Badische Anilin und Soda-fabrik at Ludwigshafen, and the investment of nearly £1,000,000 before laboratory synthesis was translated into a commercially successful industry, for it was in 1897 that the artificial indigo was put on the market. (Baeyer's first patent for the synthesis of indigo from *o*-nitro-cinnamic acid was taken out in 1880, and by 1907 there had been no less than 316 patents obtained in Germany for processes connected with the preparation of indigo.

	British East Indies.		Germany.	
	Exports.		Imports.	Exports.
	Cwt.	Value, £.	£	£
1896 .. ..	188,337	3,569,670	1,036,000	319,550
1899 .. ..	135,187	1,980,319	415,450	392,250
1902 .. ..	89,750	1,234,837	184,350	923,100
1905 .. ..	49,252	556,405	60,100	1,286,050
1908 .. ..	32,490	424,849	44,100	1,932,750
1911 .. ..	16,939	225,000	22,300	2,091,500
1913-14 ..	60,000—70,000			

In 1896 the world production of plantation indigo (100 per cent) was 6,000,000 kilograms., value £4,000,000; four-fifths of this was British, obtained from 1,500,000 acres in British India. In 1904 only 500,000 acres was under cultivation, and in 1913 only 300,000 acres.

The price of indigo (100 per cent) in 1897 was 16s. per kilogram. and in 1913 7s. per kilogram.

By varying the ingredients in the indigo synthesis many very valuable dyes related to indigo have been obtained. Thus, the chlorine and bromine substituted indigos are manufactured as *ciba* blue, brilliant indigo, and bromo indigo; again, with sulphur instead of oxygen, thio indigo-red and thio indigo-scarlet. Moreover, by using the anthracene grouping in the indigo synthesis a number of most important colours have been obtained, *e.g.* indanthrenes, of extraordinary fastness to light; alizarin indigo; algal colours (Rob. E. Schmidt), in all varieties of colour and of the greatest fastness to light. The discovery of these valuable dye-stuffs provoked zealous emulation on the part of the azo colour chemists, who responded by placing some very excellent new products on the market under the name of benzolight colours.

**Antique or Tyrian Purple** was perhaps the most highly prized of all colours in the ancient world. We know from Pliny that this dye was obtained from a rather rare snail living in the Mediterranean, and which he describes under the name of "purpurea." Paul Friedländer, of Darmstadt, succeeded in 1909 in extracting this colour from certain glands of two different species of snail—*Murex brandaris* and *Murex trunculus*—which appeared to correspond to Pliny's description of "purpurea." He removed these glands from 12,000 individual snails, developed the colour by a short exposure to sunlight, extracted it with suitable solvents, and re-crystallised it from quinoline. In this manner he obtained only 1½ grm. of the colouring matter, so that its extreme costliness, which Friedländer estimates at about £2000 a kilogram., is not surprising.

On investigating the chemical nature of this colour he found that it was identical with the already known synthetic compound 6·6'-dibrom indigo.

**Drugs and Perfumes.**—Not less remarkable are the achievements of organic synthesis in connection with pharmaceutical and perfumery products.

The production of artificial drugs and perfumes is in general only a branch of the artificial colour industry, for in many cases the raw materials are the same, whilst the methods of investigation and synthesis are of course identical, but whereas the artificial colour industry started in England, that of artificial drugs is entirely of German origin, and may be said to begin with the discovery by Liebig of chloroform in 1831 and of chloral hydrate in 1832. It was in 1869 that the chemical works of Schering, on the suggestion of O. Liebreich, produced chloral hydrate as a commercial article.

In 1887 began the discovery of artificial antipyretic drugs, the rivals of the natural quinine. The first of these was antifebrin, the properties of which were discovered accidentally in consequence of a mistake. A specimen of acetanilide in a Strassburg pharmacy was erroneously supposed to be naphthalene, and was served out as such for some pharmacological experiments by Kahn and Hepp. On being taken internally its antifebrile effect was observed. Fortunately there was enough left for analysis, and it was found that the supposed naphthalene was the long known acetanilide, which soon acquired a great vogue for this purpose. About the same time antipyrin was discovered by Knorr, who erroneously thought that it was chemically related to quinine, and that it would, therefore, not improbably possess antifebrile properties. Direct experiment showed that it did actually possess these properties in a high degree, but subsequent research showed that it was in no way chemically related to quinine. These and numerous other artificial antipyretics have been a great source of income to their inventors in consequence of the continued prevalence of influenza during the past quarter of a century.

During the period that antipyrin was protected by patent it was sold at £6 per kilogram., whilst on the expiration of the patent the price was reduced to £1 per kilogram., which still allows a good margin of profit.

These discoveries have led to the systematic study by direct experiment on animals and human beings of innumerable chemical compounds, with a view of ascertaining their physiological properties. The enormous amount of most laborious work which has been carried out in connection with synthetic drugs may be gathered from the fact that up to 1912 about 5000 artificial products had been found to possess therapeutical value of one kind or another, but of course comparatively few of these have permanently established themselves in medical practice. Time does not permit me to do more than refer briefly to some of the simpler and better known synthetic drugs.

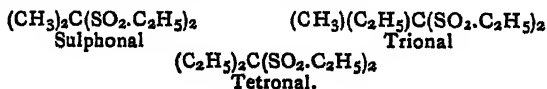
Thus, of antipyretics, which have or have had some considerable vogue, are:—Antipyrin, tolypyrin (dimethyl-tolylpyrazolone), salipyrin (antipyrin-salicylate), antipyrin mandelate (tussol, for whooping cough), neopyrin, pyramidon (three times as strong as antipyrin) (dimethyl-aminoantipyrin), antifebrin, phenacetin (cheapest antipyretic excepting antifebrin, about 6s. per kilogram., and less poisonous than antifebrin), lactophenin, lactyl- $\beta$ -phenetidine, aminophenacetin or phenocoll (also has an antiseptic action).

The above series derived from aniline affords a good illustration of the dependence of physiological properties on chemical constitution. Aniline itself is a powerful antipyretic, but is extremely poisonous, owing to its ready absorption and action on hæmoglobin. By introducing the acetyl group the toxic properties are much reduced, owing to its greater stability, although acetanilide is slowly hydrolysed with liberation of aniline, so that after a time the symptoms of aniline poisoning may supervene. The observation that acetanilide is partially oxidised in the system to  $\beta$ -aminophenol led to derivatives of the latter

being tried. Thus phenacetin has been found to possess powerful antipyretic and greatly reduced toxic effects ("Chemistry of Synthetic Drugs," P. May, 1911).

**Hypnotics.**—Sulphonal was accidentally discovered to possess hypnotic properties in connection with experiments on the transformations of sulphur compounds in the animal system. A dog, which had been dosed with the newly discovered sulphonal in Baumann's laboratory at Freiburg, i.B., was found to fall into a deep sleep.

More powerful hypnotics were found to result from introducing further ethyl groups:—



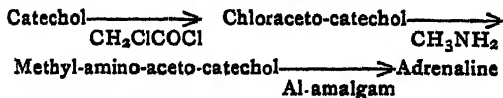
In connection with the manufacture of sulphonal I may refer to an interesting difficulty which was experienced by the Elberfeld Colour Works (Bayer und Co.) owing to the appalling smell of the mercaptan from which it is prepared, and of which Emil Fischer and Penzoldt have shown that the human nose is still capable of appreciating 1/400,000,000 mgrm. In spite of this, German thoroughness has been successful in so perfecting the apparatus in which the manufacture is carried on that no nuisance is occasioned.

Veronal (diethylbarbituric acid) (E. Fischer and Mering, patented by Merck in 1903) is one of the most widely used hypnotics. Although it was formerly supposed to be practically free from toxic properties, in recent years cases of veronal poisoning have been known to occur.

**Antineuralgics.**—Salicylic acid, one of the first drugs to be artificially prepared (Kolbe, 1860), acetyl-salicylic acid (aspirin), and salol (phenylsalicylate), though extremely simple synthetic products, are almost exclusively made in Germany, with the result that their price has now greatly increased. Even synthetic phenol, which is necessary for the above preparations, was exclusively made in Germany and kept down the price of coal-tar phenol. The price of phenol has now enormously increased from 3½d. per lb. to rs. 4d. per lb., and is likely to go higher. (*Pharm. Journal*, 1915).

**Anti gout Drugs** (uric acid solvents).—Piperazine (discovered by Hofmann in 1890), lysidine, urotropine (hexamethylene tetramine), atophane ( $\alpha$ -phenyl cinchonic acid).

**Suprarenins.**—This is of special interest. The active principle of the suprarenal glands known as adrenaline (discovered by Takamine in 1901) had for some years been found to be of great value for increasing the blood-pressure, contracting the blood-vessels, and arresting hæmorrhage. It requires the suprarenal glands of 40,000 oxen to prepare 1 kilogram. of adrenaline, but this substance has been artificially synthesised by F. Stolz, and is put on the market as suprarenine by the Höchst Colour Works. The synthesis of adrenaline may be represented thus:—



Natural adrenaline is lævo-rotatory; the synthetic can be resolved by tartrate; the lævo is fifteen times as potent as the dextro.

The German colour manufacturers are organised into two principal groups or trusts (Interessengemeinschaft):—(1) Badische Co., of Ludwigshafen; Bayer Co., of Elberfeld; Berlin Aniline Co. (2) Cassella Co., of Frankfurt; Meister, Lucius, und Brüning, of Höchst ("German Coal Tar Companies," *Textile Mercury*, Jan. 9, 1915).

The share capital of the above two groups in 1911 was £8,000,000, paying a dividend of 25·8 per cent, and probably now about £12,000,000, dividend 28 per cent.

In 1860-70 Germany imported about £2,500,000 worth



of dyes per annum, while in 1912 Germany exported about £10,000,000 and produced about £12,500,000 of dyes.

The composition of the *personnel* who carry on these German colour works is at the bottom of their success. Take the works of Messrs. Meister, Lucius, und Brüning as an example. In 1913 the composition was as follows: Workmen 7685, managers 374, expert chemists 307, technologists 74, commercial staff 611. Contrast with the above the fact that the six English factories now producing dyestuffs employ altogether only 35 chemists, whilst evidence of their relative activities is again furnished by the circumstance that between 1886 and 1900 the English firms took out only 86 patents, whereas the six principal German firms were responsible for 948 during the same period.

Having shown that these German coal-tar colour manufacturers are without rivals from the commercial point of view, I feel it to be my duty to point out also that their industry is carried on under conditions of labour which are highly creditable to the management.

This vast and highly organised industry of dyestuffs and fine chemicals, which is certainly one of the most outstanding manifestations of the modern German spirit, was formerly very dependent on England for its chief raw material, coal-tar, and it is interesting to see how effectually Germany has emancipated herself from a control which might at any time become irksome or even paralysing.

#### German Coal-tar Production.

		Coke ovens. Tons.	Gas manufacture. Tons.
1897	.. ..	52,000	—
1900	.. ..	93,000	—
1904	.. ..	277,000	225,000
1908	.. ..	632,400	300,000

In 1908 40,000 tons was still imported from England, and in 1909 18,000 tons, but 35,000 was also exported.

In 1900 the German production of coal-tar was only about one half of that produced in England, whilst by 1912 it had equalled if not surpassed the English production. Again, in 1880 Germany used 1400 tons of pure anthracene, of which only 200 tons was of German origin, whilst at the present time the 5000 tons now employed in Germany is all produced there.

The phenomenal increase in the German coal-tar production has depended on a similarly rapid development of the German iron and steel industry, which has entailed an enormous demand for metallurgical coke, in the production of which the greatest attention has been devoted by Germany to the recovery of the by-products—tar, gas, ammonia, &c.

In England the quantity of coal-tar treated was 175,000 tons in 1870, and 640,000 tons in 1880; at present over 750,000 tons is treated.

With regard to the synthetic perfume industry, the facts are in many respects essentially similar to those in connection with the artificial dyestuffs. The production of artificial perfumes, in many cases the identical substances which are produced by nature, has assumed very large proportions in Germany, the annual output being estimated at about £2,500,000. It is again particularly noteworthy that one of the first steps in the realisation of this remarkable achievement of artificially building up the natural perfumes was also made by William Henry Perkin, who in 1868 succeeded in synthesising coumarin, the highly valued odoriferous principle of the woodruff (*Asperula odorata*).

The effect of artificial synthesis on the price of natural perfumes may be gathered from the following examples:—

		Price of 1 kilogram.	
		Natural.	Synthetic.
Coumarin..	..	£25	£1 5 0
Vanillin ..	..	£50	£1 10 0
Heliotropin	..	£150	£0 10 0

(To be continued).

## BLOOD CHARCOAL AS A PURIFYING AGENT FOR ARSENIC SOLUTIONS PREVIOUS TO TITRATION.\*

By ROBERT M. CHAFIN.

WHENEVER possible, arsenic is estimated by the highly accurate and convenient method of titration with iodine. As necessary conditions, the solution must be free from other substances capable of absorbing iodine during the titration, and from colouring matter to obscure the end-points.

The laboratory of the U.S. Department of Agriculture, Washington, has been required to examine very many samples of the arsenical dipping baths now so largely used for ridding cattle of Texas-fever ticks (compare *Farmer's Bull.* 603, U.S. Dept. Agric.). The important insecticidal ingredient of these baths is an alkaline arsenite, and it is in this form that the arsenic is introduced when the baths are prepared. But with accumulation of dirt and excrement from the cattle during months of use in dipping vats, the baths become culture media for micro organisms which may either oxidise the arsenic or reduce it again, depending upon prevalent conditions (compare U.S. Dept. Agric., *Bull.* 76). In a sample of used bath therefore it is necessary to determine both actual arsenious oxide and total arsenic.

The organic matter present in used arsenical dipping baths interferes with titration by iodine in both the undesirable ways; it absorbs iodine under the conditions of the titration, thus rendering the end-points inaccurate and fugitive, and it imparts colour to the solution. An obvious first step is to acidify and filter the bath, adding also a clarifying agent. Purified kaoline or kieselguhr are only moderately beneficial, but in blood-charcoal was found an agent which, used in small amount and with brief digestion, produced water-white filtrates wherein the end-points with iodine came out sharply and permanently. Before the substance could be employed in routine analytical work it was necessary to ascertain if its well-known adsorptive and oxidative powers would affect the arsenic present (compare Rosenthaler and Turk, *Arch. Pharm.*, 1906, ccxlv., 517).

The simple plan of investigation involved treatment of measured portions of a standard arsenious acid in parallel, with and without charcoal, followed by titration with standard iodine. Approximately twentieth-normal solutions were employed, and to each 25 cc. of arsenious acid solution was added 5 cc. of 10 per cent (by weight) sulphuric acid, and 0.25 gm. blood-charcoal (if any used), previous experiments having shown this quantity to be ample for the purification of 25 cc. of very filthy dipping baths. All filtrations followed by washing were carried to a total volume of 125 cc. Arsenious oxide was titrated in presence of sodium bicarbonate. For total arsenic the 125 cc. of filtrate and washings were boiled down to 50 cc. after addition of 3.5 cc. concentrated sulphuric acid and 2 grms. potassium iodide. From the cooled solution, diluted to 250 cc., excess iodine was cautiously removed in presence of starch by a dilute solution of sodium sulphite (0.5 per cent of anhydrous salt), then acid was neutralised with sodium carbonate and bicarbonate, and after further dilution the titration was complete in the usual way.

In the table each figure for an iodine titration represents the average result from at least two closely agreeing and wholly independent tests.

From the results it is evident that blood-charcoal, though slightly adsorbing arsenious oxide from acid solution, quantitatively returns it to thorough washing, not, however, in its original state, but more or less oxidised to arsenic acid. The charcoal used, purchased as "acid-washed," was exhaustively purified with hydrochloric acid

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to free it from iron, consequently there is no reason to believe that the evident oxidative properties it displayed can be attributed to anything else than oxygen of the air likewise adsorbed by it, the power of charcoal to adsorb gases being sufficiently well known.

No.	Procedure.	Cc N/20 I per 25 cc As <sub>2</sub> O <sub>3</sub> sol		Apparent loss; cc N/20 I
		Without charcoal.	With charcoal.	
1.	Direct titration for actual As <sub>2</sub> O <sub>3</sub>	25 14	—	—
2.	50 cc. As <sub>2</sub> O <sub>3</sub> , 10 H <sub>2</sub> SO <sub>4</sub> , 0.50 grm. charcoal; made to 100 cc. in stoppered flask, mixed, and filtered after forty minutes, discarding first runnings. Titrated 50 cc. for actual As <sub>2</sub> O <sub>3</sub>	—	24.47	0.67
3.	In a 100 cc. beaker, low form, 25 cc. As <sub>2</sub> O <sub>3</sub> , 5 cc. H <sub>2</sub> SO <sub>4</sub> , 0.25 grm. charcoal; stirred cold five minutes, filtered (a), washed, and titrated for actual As <sub>2</sub> O <sub>3</sub>	—	24.97	0.17
4.	Similar to No. 3 except heated five minutes on steam bath. Titrated for actual As <sub>2</sub> O <sub>3</sub>	—	24.91	0.23
5.	Similar to No. 4 except heated for forty minutes with occasional stirring. Titrated for actual As <sub>2</sub> O <sub>3</sub>	25.15	24.74	0.40
6.	Similar to No. 5 except titrated for total arsenic	25.14	25.13	Nil

(a) The tests without charcoal were not filtered but were made directly to the desired volume.

Other similar experiments, which in view of their simplicity are not detailed, showed that (1) the amount of arsenious acid oxidised is dependent upon the amount of charcoal used as well as upon the length of heating, but not at all upon the concentration of arsenious acid (at any rate between 5 cc. and 25 cc. of twentieth normal solution in an original volume of 30 cc.); (2) arsenic acid is likewise slightly adsorbed, and likewise quantitatively returned to thorough washing.

As to the practical application of the above observations, it is believed that they may be of considerable assistance in the estimation of both arsenious and arsenic acids in a variety of substances. As a test of the decolorising power of the charcoal, 2 grms. of a sample of London purple (obtained through the courtesy of C. C. McDonnell, of the Bureau of Chemistry and stated to contain approximately 25 per cent of dye-stuff) were digested with 100 cc. dilute hydrochloric acid according to the method of the A.O.A.C. (Bureau of Chemistry, *Bull.* 107, revised), and were then treated for five minutes at 60° to 70° C. with 2 grms. blood-charcoal, being stirred most of the time. To obtain the most trying conditions, the solution was then at once filtered with suction, washing continued to a total volume of 250 cc., and the filtrate finally made to 300 cc. A 50 cc. aliquot, which is the quantity officially prescribed for each estimation—corresponding to 0.333 grm. charcoal—developed no trace of purple colour when treated with excess of either sodium carbonate or bicarbonate.

If actual arsenious oxide is to be determined it is of course necessary to obtain a "correction for oxidation" on the sample of charcoal to be employed, under the precise set of conditions which will prevail in the analysis.

The writer has previously recommended the use of blood-charcoal in the assay of arsenical dips (U.S. Dept. Agric., *Bull.* 76), noting the necessity for a correction, but at that time had reason to believe—and so implied—that it was chiefly attributable to adsorption. The precise cause of the phenomenon was not of prime importance in a purely technical paper, but in the interests of scientific accuracy the matter has since received this special study.

## A GARDEN OF SERPENTS.

By JACQUES BOYER.

In the Serotherapeutic Institute of Brazil, which occupies a tract of 700 acres at Butantan, Dr. Vital Brazil produces serums for the cure and prevention of the effects of snake bites. The snakes used in preparing the serums are kept in a small park, containing numerous dome-shaped shelters, which is surrounded by a wall and a ditch filled with water. Other specimens are kept in a similar park, near the main building, in order to study their habits, favourite food, the very diverse venomous properties of various species, and the best method of escaping their attacks. The hot and moist forests of Brazil swarm with venomous serpents, but the slightest noise alarms the peaceful and timid reptiles, which attack only those persons and animals that tread on them or destroy their lairs. The principal families are the Bothrops and the Crotales, or rattlesnakes. The Bothrops venom decomposes the blood and produces internal hæmorrhage, with intense congestion of the liver, kidneys, and brain, while the venom of the Crotales paralyses the respiration, circulation, and vision, and usually causes death within twenty-four hours. Each venom requires its special antidote. Dr. Brazil prepares a serum for each, and also a polyvalent or compound serum, which is effective against all Brazilian snake venoms, for use when the species of the attacking snake is unknown.

The serums are obtained from young and sound horses and asses, which receive, at intervals of five or six days, injections of venom, increasing from one-twentieth mgrm. to 1 grm. A year's treatment is required to produce perfect immunity and an effective serum. The polyvalent serum is obtained by injecting the venoms of Bothrops and Crotales alternately. The animals thus immunised furnish anti-venom serum for a long time, if they receive a fresh injection of venom after each extraction of serum. Tubes of serum, with hypodermic syringes, are sent gratuitously to hospitals, municipalities, and poor patients. Others are sold at low prices or exchanged for live snakes. In 1913 about 900 tubes of rattlesnake serum, 800 of Bothrops serum, and 4500 of polyvalent serum were distributed, and 4500 snakes were received. Serums for pest, diphtheria, and tetanus also are produced by the usual methods.

In the course of his study of Brazilian serpents, Dr. Vital Brazil has discovered a non-venomous constrictor snake, the *musurana*, which is naturally immune to snake venom, and which kills venomous snakes by crushing them in its coils and then devours them.

It is a remarkable fact that the serums prepared at Lille by Dr. Calmette, the originator of the serum treatment for snake bites, are powerless against the venom of Brazilian serpents.—*Scientific American*, cxii., No. 20.

## INTERNATIONAL INSTITUTE OF AGRICULTURE.

### Bulletin of Agricultural and Commercial Statistics.

THE May number of the above Bulletin published by the International Institute of Agriculture (Rome) confirms the information contained in the preceding month's number regarding the production of wheat, rice, and cotton in India, with the addition of the figures for the sesamum crop in the same country, which is estimated at 5,874,784 quintals for 1914-15, against 4,097,718 in 1913-14, or 143.4 per cent.

Tables follow with data on areas sown with wheat, rye, barley, oats, and maize. Among new data are the areas sown in Spain up to the end of March, estimated at 3,959,652 hectares for wheat, 1,490,466 for barley, and 493,461 for oats, or 101 per cent, 108 per cent, and 93.5

per cent, respectively, of the areas last year. For maize the areas sown in Italy amounts to 1,600,000 hectares, or 101.7 per cent of that in 1914.

Reports are next published regarding cereal crop conditions in the different countries on May 1, the conditions being generally good or average for most of the countries which sent word (Austria, Hungary, France, Great Britain and Ireland, Italy, Switzerland, Canada, Japan, Algeria, Egypt, and Turin). In the African countries harvest has already begun.

The Bulletin gives information for certain countries on the appearance and progress of the cotton, rape, potato, tobacco, vine, olive, and sugar-beet crops, and also on the sericultural campaign.

For the Southern Hemisphere crops the data on the second estimate for Argentina of wheat, oats, and linseed are shown, which vary appreciably from those published in the March Bulletin. The wheat crop for 1914-15 is now estimated at 48,504,000 quintals, or 156 per cent of that in 1913-14; the oats crop at 9,201,000 (100.8 per cent), and the linseed crop at 12,424,000 (124.9 per cent).

The production figure for wheat in Australia is also modified to 6,782,667 quintals, against 28,126,139 in 1913-14, or 24.1 per cent of the latter.

### WELSH NOTES.

(By Our Special Correspondent).

THE trade of Swansea Port experienced a strong revival during the past week, and notwithstanding the comparative inactivity over the Whitsun holidays an increased tonnage of 10,000 tons was registered as compared with the corresponding week of last year. The unusual quietness of the import trade was more than counterbalanced by a very large export of patent fuel. The imports included 550 tons of iron ore from France, 1100 tons of pig-iron, 1101 tons zinc ore, and 255 tons of scrap steel from Spain, and 2500 tons zinc ore from Italy. The shipments of tin-plates amounted to 89,360 boxes; received from works, 66,210 boxes; stocks in dock warehouses and vans, 308,185 boxes, compared with 331,335 boxes the preceding week and 260,077 boxes at the corresponding date last year. Patent fuel exports amounted to 20,666 tons.

Trade at the Port Talbot Docks fell off considerably over the Whitsun holidays, although the week started with great promise. Imports included pig-iron 873 tons, and 150 tons pitch, whilst 4000 tons of patent fuel were shipped.

The Swansea Valley industries brightened up considerably on the heels of the holiday. The Landore blast-furnaces worked well, pig-iron being in heavy demand, and all steel-works were working at high pressure. In the copper trade great activity was shown, whilst the tinplate trade showed a slight improvement, with the exception of the bar mills. Spelter factories were busy, all departments being constantly at work, and the demand was pressing. Before the outbreak of the war spelter was £25 per ton, but it has now risen to over £70. Trade was good in safety-fuse and lead-piping. The Mond Nickel Works, the Mannesmann Tube Works, and the Metal Extraction Works were fully occupied, whilst the engineering and fitting shops and iron and brass foundries were as active as ever. Sulphuric acid factories were in a very quiet state.

The Siemens and Bessemer furnaces were lighted up at the Dowlais works in readiness for Tuesday morning, but the blast-furnaces had a check for a few days for renewal of some part of the plant. In the Goat Mill large orders for steel rails were rolled off, which occupied a good part of the week, the mill not finishing until late on Saturday. Steel sleepers and steel bars were also produced. In the Big Mill sole plates, fish plates, and light rails for tramways composed the bulk of output, and the mill worked on until a late hour on Saturday.

Messrs. Baldwin, Limited, held a confirmatory meeting during the week regarding the Port Talbot Steel Works merge, when the proposal was confirmed. The directorate will be increased from nine to twelve.

Just at present it is pleasing to note that the steel rail market is firm with an upward tendency, and makers seem to be not in the least distressed at the prevalent lack of new business. A small order for India—3000 tons for the Nizam's railway—has gone to the Dowlais Mills. Some considerable Australian business is shortly to be placed, and the general expectation is that this will go to the new steel works at Broken Hill. The Pennsylvanian order for about 140,000 tons has not yet been given out.

In their report for the year 1914, the directors of the well-known Swansea undertaking, the English Crown Spelter Co., Limited, do not give any information as to the general state of this important industry. As I remarked earlier in this column, spelter has risen tremendously in price since the outbreak of the war, and the firm with its mines in Italy and its own works in Swansea should be in a position to do exceptionally well. It remains to be seen whether the fact that Italy has entered the arena of war will affect operations at the mines in Lombardy, which is near the war area. The company show a profit for 1914 of £10,600, compared with £4000 in the previous year, and, besides maintaining a dividend of 10 per cent, the directors apply £2500 to reserve and suspense account, making that fund £22,500, and carrying forward £728. The report issued by the company shows that during 1914 7535 tons of raw calamine and blende were raised from the mines, and that 11,775 tons of ores were treated in the dressing works. These produced 8823 tons of calcined calamine and blende, net dry weight.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, May 20, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Corpuscular Radiation Liberated in Vapours by Homogeneous X-radiation." By H. MOORE.

"Absorption in Lead of  $\gamma$ -Rays emitted by Radium B and Radium C." By H. RICHARDSON.

1. The absorption curves in lead of the radiations emitted by radium B and radium C have been determined and analysed.

2. In addition to the penetrating type of radiation for which  $\mu = 0.5$  (cm.  $^{-1}$ ) in lead, radium C has been found to emit soft types, for which  $\mu = 46$ ,  $\mu = 6.0$ , and  $\mu = 1.5$ , and which are practically absorbed by 1.5 cm. of lead.

3. The analysis of the radium B absorption curve shows that in addition to the radiation  $\mu = 40$  in aluminium, the rays emitted consist of three types for which  $\mu = 46$ ,  $\mu = 6.0$ , and  $\mu = 1.5$  for lead. The close similarity of this latter radiation with that of the soft portion emitted by radium C, already observed by Rutherford and Andrade, has been established.

4. The absorption of the radiations in different elements has been examined and the bearing of the results discussed. No evidence of anomalous absorption has been found in the case of the penetrating radiations.

"Application of Interference Methods to the Study of the Origin of Certain Spectrum Lines." By T. R. MERTON.

By measuring the limiting orders at which interference can be detected for different radiations, certain deductions may be made as to the mass of the luminous particles and the temperature of the source. If the only circumstance which could possibly influence the width of spectrum lines at low pressures were the Doppler effect due to the motion

of the luminous particles in the line of sight, the relative masses of particles emitting radiations from the same source of light might be calculated. As, however, there is reason to doubt the validity of this assumption under certain conditions, the conclusions which may be drawn with certainty from measurements of this kind are an inferior limit for the mass of the luminous particles if the temperature of the source is known, or a superior limit to the temperature if the mass of the luminous particles is assumed.

It is shown in the paper that the flame lines of calcium, strontium, and barium are probably due to molecules, whilst the H and K lines of calcium are to be attributed to calcium atoms. As the flame lines are members of series, it must be recognised that radiations from molecules may give rise to line series as well as band spectra. Lines of the two spectra of argon have been investigated. The width of the lines of the red spectrum would appear to be accounted for by the Doppler effect. The lines of the blue spectrum are very broad in comparison with those of the red spectrum, and a satisfactory explanation of this has not been found. Spectrum lines of the "arc" type are broadened when condensed discharges are used as the method of excitation, but the difference in width of the lines in the blue and red spectra of argon is of another order of magnitude.

The band spectrum associated with helium has been found to be enhanced when the gas is cooled to the temperature of liquid air, which might justify the suspicion that more than one atom was concerned in its production, but a comparison of the width of the lines in the band spectrum with the ordinary helium lines makes it extremely probable that the band spectrum is due to atomic helium.

#### PHYSICAL SOCIETY.

Ordinary Meeting, May 28, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER "On Numerical Relationships between Electronic and Atomic Constants" was read by Dr. H. S. ALLEN, M.A.

It has been pointed out by Jeans that  $hc$ , where  $h$  is Planck's constant and  $c$  is the velocity of light, has the same physical dimensions as the square of an electric charge. Lewis and Adams have suggested a relation between these quantities of the form—

$$ch = \sqrt{\frac{8\pi^2}{15}} (4\pi e)^2.$$

This may be written—

$$\frac{2\pi e^2}{hc} = \frac{(15/\pi^2)^{1/2}}{(4\pi)^2} = q;$$

where  $q$  is  $7.28077 \times 10^{-3}$ . The square of this numerical constant is  $\beta = 5.30096 \times 10^{-5}$ . The charge  $e$  on an electron in E.S.U. is found to be, within 0.1 per cent,  $9\beta \times 10^6$ . The ratio  $e/m$  of the charge to the mass is found to be  $\beta \times 10^{22}$ , with the same order of accuracy. The occurrence of powers of 10 in these expressions may be accidental or may depend on the way in which the units of length, mass, and time were originally defined. Derived quantities, depending on  $e$ ,  $m$ , and  $c$ , can be expressed in terms of simple integers (2, 3, or 4), powers of 10,  $\beta$ , and  $\pi$ . The "atomic mass of an electron" is approximately  $10\beta$ .

#### DISCUSSION.

Prof. O. W. RICHARDSON said it was curious that the value of  $e$  and  $e/m$  should happen to be simple multiples of the quantity  $\beta$ . These two quantities were the key to the situation, as the other relations followed more or less directly from them.

Mr. S. D. CHALMERS said it was possible almost with any set of quantities to obtain striking numerical relationships. It was only when a physical significance was sought

for that it could be seen whether they were anything but coincidental.

Dr. W. WILSON said that if the units of mass, length, temperature difference, &c., were so chosen as to make the universal constants such as Planck's  $h$ , the gravitation constant, &c., each equal to unity, the unit of mass which had to be adopted was  $\beta$  gm.

Prof. ZELENY emphasised the importance of searching for the physical significance attached to these relationships.

A paper "On a Method of Calculating the Absorption Coefficients of Homogeneous X-Radiation" was read by Mr. H. MOORE.

The action of X-radiation when passing through a gas is to liberate electrons from the gas. The number of electrons emitted by any atom in a beam of X-rays is proportional to the fourth-power of its atomic weight (or possibly its atomic number). (Moore, *Proc. Roy. Soc.*, May, 1915.) Thus, equal numbers of atoms of different elements, when subjected to similar X-ray beams, will liberate amounts of electronic radiation proportional to the fourth powers of the atomic weights of the elements.

The absorption coefficients are proportional to the amounts of electronic radiation liberated, and, therefore, the absorptions of two elements, when equal numbers of atoms are present, will be proportional to the fourth powers of their atomic weights.

The corpuscular radiation liberated in the vapour of an element if it could be obtained as a monatomic vapour at 76 cms. can be expressed as  $1.05 \times 10^5 \times (\text{atomic weight})^4$ , taking the corpuscular radiation in air as unity. The absorption coefficient of such a vapour would, therefore, be this number of times the coefficient of absorption of air for the same type of X-radiation. The absorption of any element is proportional to the number of atoms present, and having calculated the absorption in a hypothetical vapour of this type, the absorption in the same element in any condition can be calculated by a simple density law.

This is done in the paper for several elements (metals), and also, assuming an additive law, it has been calculated for some compounds. The agreement between the calculated values and the values obtained by different observers by direct experiment is quite close over a considerable range of radiations and absorbers. When, however, the atomic weight of the absorber is higher than that of the radiator, so that the K series is absent from any secondary radiation excited in the absorber, the agreement ceases. A possible explanation of this is suggested in the paper.

#### DISCUSSION.

Prof. O. W. RICHARDSON thought the paper made a considerable addition to our knowledge of the process of ionisation by X-rays. The primary rays in being absorbed produce some ionisation, and, in addition, excite secondary radiation, which in turn produces more ions. The paper helps to make clear the part played by these two causes in the production of the total ionisation.

Dr. S. RUSSELL felt that the paper conveyed the impression that one would find in practice the same value for the absorption coefficient as obtained by calculation. The phenomenon of selective absorption must surely set severe limits to the range of wave-length over which these relations hold. This range should be specified. How would the author calculate the absorption coefficients, say, for aluminium and water? If there were no selective absorption  $\lambda/\rho$  should be constant, but he had recently found it to vary over a wide range.

Prof. NICHOLSON said the results were of interest to those engaged in the attempt to construct models of atoms and molecules. The phenomena appeared to be atomic in nature, thus bearing out the idea brought forward by Bragg that the atom preserves its identity in the molecule. In connection with the law connecting the absorption with the fourth power of the atomic weight, it would be interesting to know whether it was really the atomic weight or the atomic number that should be employed.

The AUTHOR replied as follows:—The formula should only be used where all the types of radiation excited in air are also excited in the material. He had had considerable trouble in getting reliable coefficients owing to the large and uncertain scattering corrections which had to be applied. In one case he believed an observed value of 0.42 had to be corrected to 0.2 or less. He had calculated some coefficients for gases, and with  $\text{SO}_2$  the agreement was as good as for solids. It should be possible to calculate the true absorption coefficient for water and aluminium, but he could not say how near these would be to values actually determined on account of the uncertain scattering. He had experiments in progress which should determine whether the atomic weight or the atomic number was the significant quantity.

"Two Experiments Illustrating Novel Properties of the Electron Currents from Hot Metals" were shown by Prof. O. W. RICHARDSON, M.A., D.Sc., F.R.S.

The first experiment demonstrates the cooling of a tungsten filament when an electron current is allowed to flow from its surface. This effect is analogous to the cooling due to latent heat when a liquid evaporates, or to the similar phenomenon due to the heat of reaction when a gas is emitted by chemical decomposition of a solid.

An experimental lamp containing a fine filament of double tungsten is placed in one arm of a balanced Wheatstone bridge actuated by the current which heats the wire. When the electron current is allowed to flow, by completing a side circuit from an electrode inside the lamp to a point in the adjacent arm of the bridge, the galvanometer is deflected in a direction which corresponds to a reduction of the resistance (and temperature) of the hot filament. The precautions necessary to eliminate fully disturbances due to various subsidiary phenomena are considered in papers by H. L. COOKE and the speaker in the *Phil. Mag.*, 1913, xxv., 624, and xxvi., 472.

The second experiment, in which a similar experimental lamp is used, demonstrates the flow of electron currents from a hot filament to a surrounding cylinder against various opposing P.D.s up to about 1 volt. On account of the large currents from tungsten this effect can easily be shown on a galvanometer. The data can be used to find the velocities of the emitted electrons (cf., *Phil. Mag.*, xvi., 353; xvii., 890; xviii., 681).

"A Short Account of Recent Experiments on High Permeability in Iron" was given by Prof. ERNEST WILSON.

1. When iron is subjected to a strong magnetic force it has the effect of reducing the permeability and increasing the hysteresis loss for given values of the magnetic induction. The effect can be largely removed by careful demagnetisation. It was thought that the earth's magnetic force might also have a polarising influence upon exposed iron, and an effort has been made to remove it by placing the specimen in a magnetic shield, and carefully demagnetising it. (*Roy. Soc. Proc.*, A., 1914, xc., 179.) The permeability corresponding to small values of the magnetic induction is thereby considerably increased, and the hysteresis loss diminished. After a long period of rest in the shield the permeability has somewhat diminished, and on taking the specimen out of the shield it maintains its high value.

2. Next as regards higher forces. The specimen in this case is not shielded, but is subjected to a magnetising force during the time that it is allowed to cool through the temperature of recalcence. Either with an alternating (*Physical Review*, second series, April, 1913, i., No. 4) or steady (*Roy. Soc. Proc.*, A., xc., 343; also *Roy. Soc. Proc.*, xci., 104) magnetic force a maximum value of the permeability of over 10,000 is obtained.

In these experiments the material has been tested on the form of laminated squares or rings. With straight strips 8 cms. long, 1.5 cms. wide, and 0.053 cm. thick, built into the form of test pieces, the effect, though pro-

duced, could not be maintained, and the specimen with ordinary handling was reduced to the normal state.

"An Experiment Showing the Difference in Width of the Spectrum Lines of Neon and Hydrogen" was shown by Mr. T. R. MERTON.

For accurate measurements of the widths of spectrum lines an interference method must be employed, in which the optical difference of path between the interfering beams can be varied, the widths being calculated from the limiting difference of path at which interference fringes can be seen. By "crossing" a Fabry and Perot etalon with a single prism spectroscopic it is possible to discriminate between lines arising from different elements, by the "visibility of the fringes." In the experiment shown a vacuum tube containing neon and hydrogen is examined in this way. The neon lines being narrow show sharp interference fringes, but for the hydrogen lines, which are broader, the limiting order at which interference can be seen is too low for fringes to be visible.

Mr. R. S. WHIPPLE expressed the thanks of the Society to Profs. Richardson and Nicholson for their kind invitation to King's College, and for the interesting and instructive programme which had been submitted.

(NOTE.—On account of the lateness of the hour, the Chairman did not invite discussion on the last three papers).

#### FARADAY SOCIETY.

Ordinary Meeting, May 11, 1915.

Sir ROBERT HADFIELD, F.R.S., President, in the Chair.

PROF. ALFRED W. PORTER, F.R.S., read a paper "On Von Babo's Law and Kirchhoff's Equation for the Latent Heat of Dilution."

The following are the chief points in the paper:—

1. Accurate formulæ are found for the heats of dilution (both reversible and irreversible) for a solution of any concentration at any hydrostatic pressure.

2. A sufficiently accurate formula is obtained connecting the heat of dilution with vapour pressures. Von Babo's law is discussed in this connection.

3. It is shown that, at any rate for sugar solutions,—

$$\log \frac{\pi}{\pi_0} = \frac{n}{N-an} \text{ approximately,}$$

where  $a$  is the hydration factor of the solute.

4. It is emphasised that  $N-an$  cannot be interpreted as the number of effective molecules of solvent in the solution on account of the association of the solvent molecules with one another. For example, in the case of water the association is almost certainly between 2 and 3. Hence the actual number of solvent molecules in the solution which are unattached to solute is between  $\frac{N}{2} - an$  and

$\frac{N}{3} - an$ ; because  $N$  is the number of molecules of solvent reckoned as in the vapour state, and steam is not associated.

Mr. D. ORSON WOOD, B.Sc., A.R.C.Sc., read a paper on "The Vapour Pressure of Concentrated Sugar Solutions." (This paper will be inserted in full).

A paper by Mr. F. J. HARLOW, B.Sc., A.R.C.Sc., and Mr. R. S. WILLOWS, M.A., D.Sc., on "A Simple Method of Deriving the Gibbs Adsorption Formula" was read by Mr. Harlow.

The usual method of deriving the Gibbs adsorption formula involves the use of chemical potential. As students find a difficulty in understanding this, a simple method of obtaining the formula is given which involves only elementary thermodynamics.

Mr. F. H. CAMPBELL, M.Sc. (Melbourne), communicated a paper entitled "The Vapour Pressures and Specific Volumes of Binary Mixtures of Volatile with Non-volatile Liquids." (This paper will be inserted in full).



Mr. R. H. CALLOW (Liverpool) communicated a paper on "*Reaction Velocity in Viscous Media*."

The reaction considered was the hydrolysis of methyl acetate in gelatin water mixtures by NaOH and HCl. Conductivity experiments on the alkaline hydrolysis failed to give satisfactory results owing to the hydrolysis of the Na salt of gelatin. The acid hydrolysis gave a series of velocity constants which showed a diminution as the gelatin concentration increased. The change in the velocity constant was small compared with the change in the viscosity; e.g., the velocity constant for the reaction proceeding in a set jelly was only about 10 per cent less than that in the case where no gelatin was present. The curves showing the relation between the velocity constant and the viscosity and fluidity of the mixtures do not appear to obey any simple relation. The fall in the velocity constant is supposed to be due partly to the neutralisation of the HCl by the gelatin, and partly to the viscosity. The author suggests that the effect of the viscosity is given either by a reciprocal relation such as  $\eta(K-c) = \text{const.}$ , where  $c$  is a constant, or by an exponential function.

Mr. K. C. BROWNING, M.A., and Mr. C. T. SYMONS, B.A. (Ceylon), sent in a description of "*A Convenient Thermostat for Accurate Specific Gravity Determinations and a Gas Pressure Regulator*." (This paper will be inserted in full).

Mr. E. J. HARTUNG, B.Sc. (Melbourne), communicated a paper on "*A New Method for Determining the Specific Heats of Liquids*." (This paper will be inserted in full).

Mr. J. S. ANDERSON, M.A., B.Sc., Ph.D. (Birmingham), contributed a paper on "*An Electro-magnetic Vacuum Balance*."

The balance was designed to allow of weighings being carried out *in vacuo*. The principle involved is that of the well-known Kelvin balance for "weighing" electrical currents. One of the scale-pans of an ordinary balance is replaced by a circular coil of wire which is movable between two larger fixed coils of wire, the three coils having a common vertical axis. The coils are so connected that, when a current of electricity is passed through them in series, the movable coil is attracted by the lower, and repelled by the upper, fixed coil. These attractive and repulsive forces, which may be increased or decreased by varying the electrical current, are made use of to counter-balance the action of gravity on the substance to be weighed in the scale-pan hanging from the other end of the balance-beam. Should the weight of the substance vary from time to time, the variations in weight can be determined by altering the current through the coils until equality of the forces acting on the two ends of the balance-beam is obtained. The balance must first, of course, be calibrated.

The base of the balance is fixed to a glass plate over which a bell-jar is placed, thus allowing of the apparatus being evacuated. Two terminals, which serve for leading in the current for the coils, pass through the glass plate.

The arrestment is controlled by an electro-magnetic device operated from outside the balance. Attached to a lever at the back of the balance are two iron rods which can move freely in a vertical direction inside two solenoids. When an electrical current is passed through one solenoid the balance-beam is released; when passed through the other solenoid, the beam is fixed. As soon as the beam is either released or fixed, the current may be switched off without altering the position of the beam.

A difference in weight of 0.35 to 0.7 mgrm. could easily be detected when use was made of an ampère-meter which was not very sensitive. The balance is specially suited for measuring changes in the weights of substances *in vacuo*. Measurements were made of the velocity of absorption of water-vapour by silicic acid gels.

Mr. E. B. R. PRIDEAUX, M.A., D.Sc. (Nottingham), sent in a "*Note on the Neutralisation Curve of Boric Acid*."

The hydron concentrations of boric acid at various

degrees of neutralisation may be calculated with one dissociation constant. If that of Walker  $K = 1.7 \times 10^{-9}$  is used, the calculated acidities over the greater part of the curve are too high as compared with the experimental values of Sørensen. A modified dissociation constant  $K = 4.5 \times 10^{-10}$  derived from these values gives a good agreement, except that the acidity is too low at the acid end.

These differences are accounted for by the formation of complexes in solution.

Mr. NORMAN MURRAY BELL (St. Andrews), contributed a paper "*On the Anodic Solution of Lead*." (This paper will be inserted in full).

Mr. F. C. THOMPSON, M.Met., B.Sc. (Sheffield), communicated a paper on "*The Elastic Strength of Metals*."

In a normal pure metal the inter-crystalline boundaries are by far the strongest part of the whole. This rather unexpected fact has recently been explained by assuming that a hard vitreous modification of the metal exists between the crystal grains, the strength of which "cement" is sufficiently great to stiffen up the whole mass. This explanation, however, necessitates the assumption of a tensile strength for the cement of an almost impossible order.

On the assumption that surface tension effects are to be expected in the "glassy" films, an expression for the elastic limit of a pure metal is derived.

It—

$E$  is the E.L. in dynes per sq. cm.,  
 $n$  is the number of crystals per cm.,  
 $T$  is the surface tension of the films, and  
 $d$  is their thickness,

$$E = 1.5n \frac{T}{d} \quad \dots \dots \dots (i.).$$

The equation agrees well with recent work on the yield-point in metals and on their mechanical properties at high temperatures.

Bars of pure lead, tin, zinc, antimony, silver, copper, iron, and nickel were used to test the relationship, the iron being used in five different conditions.

Although this equation governs the elastic limits of metals, the maximum stress and Brinell hardness are dependent on other terms, chiefly the "intrinsic pressure," with the result that alterations may be made in the elastic limit of a material without appreciable effect on its hardness.

The electrical resistance of a normal metal  $\rho$  is shown by measurements of the samples of treated iron to be the sum of the resistance of the crystalline material  $\rho_1$ , and an added resistance due to the crystalline junctions, so that if  $n$  is the number of the latter per cm., and  $R$  their resistance—

$$\rho = \rho_1 + nR \quad \dots \dots \dots (ii.).$$

Thus from (i.) and (ii.)—

$$d = \frac{1.5T}{E} \cdot \frac{\rho - \rho_1}{R} \quad \dots \dots \dots (iii.),$$

which allows  $d$ , the thickness of the film of under-cooled metal between the crystals, to be calculated.

Results are obtained for a pure iron, and discussed in their bearing on the theories of the origin of the films.

Mr. LESLIE AITCHISON, M.Met. (Sheffield), sent in a paper entitled "*Experiments on the Influence of Composition upon the Corrosion of Steel*."

The work embodied in this paper has been performed upon a series of some sixty steels, comprising (i.) plain carbon steels, (ii.) steels containing a constant proportion of carbon and varying proportions of tungsten, chromium, cobalt, or vanadium, (iii.) steels with constant proportions of tungsten, chromium, vanadium, manganese, or nickel, and (iv.) some steels containing copper. The attacks recorded are those of (i.) 3 per cent sodium chloride, (ii.) 10 per cent sulphuric acid, and (iii.) 1 per cent sulphuric acid. The work shows that in the case of the pure carbon steels an increase of the carbon produced at first a fall of

the corrosion, and then a rise to a well-marked maximum at 0.9 per cent of carbon. The addition of varying proportions of tungsten to a series of steels containing about 0.7 per cent of carbon has produced a definite increase of the corrosion throughout. Varying percentages of cobalt added to a similar series have produced an increase of the corrosion with the presence of smaller quantities of cobalt, and in all cases a gradual fall of corrosion with a rise of cobalt. In the two acid solutions the higher proportions have produced a corrodibility less than that for the corresponding pure carbon steel. The presence of vanadium in varying proportions has resulted in a definite increase of the corrodibility. The addition of chromium produces an increase of the corrosion up to 5 per cent, then a remarkable fall to a material containing 10 per cent of chromium, which is quite non-corrodible in brine, and almost so in 1 per cent sulphuric acid, but which is highly corrodible in 10 per cent acid.

In the third series the percentages of the third elements present are fairly low, and the addition in all five cases has produced an increased corrosion in brine. In the 1 per cent acid, tungsten and nickel have (in general) produced a decrease, whilst vanadium and manganese show a tendency to produce an increase of the corrosion. In the 10 per cent acid, tungsten and nickel generally produce a decrease, whilst chromium, manganese, and vanadium show a distinct increase. The steels containing copper show an increased corrosion in brine and 1 per cent acid, but a decreased corrosion in 10 per cent acid, after the copper has risen above 1 per cent.

In general, it is suggested fairly strongly that anything tending to the production of finer pearlite in steels, but which does not produce a mixture of carbide and solid solution (as distinct from a eutectic), causes an increase in the corrosion of the material. The relation of the presence of carbides to the corrosion is also discussed. Further conclusions to be drawn from the work are postponed until other experiments on the question have been published, these being promised for the near future.

The discussion on this paper was postponed until the autumn, when a general discussion will be held on "*The Corrosion of Metals—Ferrous and Non-ferrous.*"

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 2, 1915.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

Messrs. Edward Theodore Brewis, William McDonnell Mackey, and Percival John Fryer were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Eric Keightley Rideal and Arthur Sidney Carlos.

The following papers were read:—

"*The Composition of Dutch Cheese, and the System of Cheese Control in the Netherlands.*" By J. J. L. VAN RYN, Ph.D.

A review is given on the result of the analyses of a great number of cheeses made under control, proving that full-cream Dutch cheese does not contain less than 45 per cent of fat in the dry substance, and showing the relationship between fat in milk and fat in cheese.

"*Estimation of Starch in Cocoa by the use of Taká-diastase.*" By CECIL REVIS and H. R. BURNETT.

The authors show that the only accurate method of estimating starch in cocoa is by the use of taká-diastase. All other methods show an apparent percentage of starch in cocoa-shell, which does not actually exist.

The use of taká-diastase shows it to be free from starch. A quick and easy method for clearing the solution for polarimetric work is described.

"*The Volumetric Estimation of Ferrocyanides.*" By BERTRAM CAMPBELL, B.Sc., A.I.C.

A method is described which depends upon the destruction of the ferrocyanogen complex by sulphuric acid and the subsequent estimation of the iron volumetrically by potassium permanganate. It is specially applicable for the evaluation of the degree of purity of ferrocyanides which are known to contain iron in no other form.

"*Corean Beeswax.*" By SEIICHI UENO.

The author points out that beeswax was produced in Corea in considerable quantities at a comparatively early period. Statistics are given of the quantities produced in various provinces during the year 1912.

A table of analytical constants is given for samples of pure Corean beeswax which were exhibited at the Taisho Exhibition at Tokyo last year.

The determination of the acid and saponification values was made by Bohrish and Kürscher's modified process (*Pharm. Zentralh.*, 1910, xxv., 20).

The result showed that the characteristics of Corean and Japanese beeswaxes are similar to each other, and that they also resemble certain Indian beeswaxes, referred to in Lewkowitch's "*Oils, Fats, and Waxes*" (1914, fifth ed., ii). The Oriental beeswaxes, secreted by the three species of bees mentioned in the paper, are different in their character from European and American beeswaxes, which are secreted by *Apis mellifica*, L.

"*Note on the Detection of Beta-Naphthol in Disinfectants.*" By R. BODMER, F.I.C.

Richmond (*Analyst*, 1907, xxxii., 151) recommends a diazotised benzidine solution for the detection of  $\beta$ -naphthol in milk. The author has tried this test on lysol and similar cresylic acid preparations. A 1 per cent solution of lysol, free from  $\beta$ -naphthol, gives, with a few drops of the benzidine reagent, an orange colouration. On adding as little as 0.2 per cent of  $\beta$ -naphthol to the same lysol and taking a 1 per cent solution a distinct ruby red colouration is produced (easily distinguishable from the orange solution of the pure lysol) on the addition of a few drops of the benzidine solution.

A diazotised solution of phenylhydrazine was also tried, but the reaction was not so sensitive as with the benzidine reagent.

J. Katayama and B. Ikeda (*Analyst*, 1915, xl., 164) recommend a very weak solution of sodium nitrite to be added to the solution of  $\beta$ -naphthol with sulphuric acid, a purple colour being formed. This test does not answer satisfactorily in the presence of cresylic acid. Separation of  $\beta$ -naphthol from cresylic acid by fractional distillation or otherwise is extremely difficult.

The Biochemical Society.—A meeting of this Society will be held at the Rothamsted Experimental Station, Harpenden, Herts, on Saturday, June 12, 1915. The Director and staff of the Experimental Station will show members round the various plots during the morning and the afternoon. There will be an interval for a light luncheon during the visit to the fields, and tea will be in the Laboratory about 4.30 p.m. Communications will be made as follows:—

W. E. Brencley.—Effect of the Concentration of Nutrient Solutions upon the Growth of Plants in Water Culture.

W. A. Davis.—Periodic Variation of the Sugars in the Foliage Leaves of Plants during the Day and Night.

W. A. Davis and G. C. Sawyer.—Variation of the Starch Content of the Potato Leaf during Day and Night and its Relation to the Sugars present.

E. H. Richards.—Loss of Nitrogen during the Bacterial Decomposition of the Nitrogen Compounds of Animal Excretions.

A. Appleyard.—The  $\text{CO}_2/\text{O}_2$  Ratio in Soil Oxidations.

W. Weir.—Effect of Soluble Humus on Plant Growth.

E. Horton. Methods for the Extraction of Organic Compounds from Soil.

J. Prescott and E. J. Russell.—Reaction between Soil Phosphates and Dilute Acids.

## NOTICES OF BOOKS.

*X-Rays and Crystal Structure.* By W. H. BRAGG, M.A., D.Sc., F.R.S., and W. L. BRAGG, B.A. London: G. Bell and Sons, Ltd. 1915.

It is remarkable that two branches of science so widely separated as crystallography and radiology should become unexpectedly linked together to their mutual advancement. The suggestion by Dr. Laue, of Zurich, followed as it immediately was by the practical demonstration of its accuracy by Friedrich and Knipping, has, in fact, constituted one of the greatest advances that has been made within the last few years in either of the sciences.

In the hands of Prof. Bragg and his son, W. L. Bragg, the new knowledge has given rise to an investigation which has thrown a flood of light both upon the mechanics of crystal structure and upon the nature of X-rays. In crystallography the somewhat obscure though quite legitimate theories of lattice spacing has been demonstrated photographically in a remarkable manner; the two photographs reproduced in the introduction (Plate I.) showing the patterns produced by the diffraction of an X-ray beam after passing through plates of nickel sulphate and of beryl, carry more conviction to the mind as to the beautiful symmetry of crystal structure than would many pages of intricate calculations. The object of the authors has been to set out clearly and briefly the facts and principles relating to X-rays and crystals, and to follow this with a detailed account of their experimental work upon the subject; this latter section occupies the larger portion of the book.

The principal gain of the authors' researches appears to lie in their striking confirmation of the conclusions reached by many physicists, that X-rays are electromagnetic disturbances of the same nature as light, heat, and electricity, their novel properties resulting solely from their almost incredibly short wave-length.

Using tubes provided with suitable anti-cathodes the authors have produced beams of homogeneous X-rays, and have been able to measure their wave-length with an accuracy comparable to the spectroscopic analysis of luminous radiations.

It is found that the most usual forms of X-rays, "hard and soft" rays, have wave-lengths that fall between 0.5 and 1.5 Angstrom units.

To note briefly the contents of the book which is intended as an introduction to the study of this interesting subject.

The first chapter gives an exposition of the theory of the ruled grating as applied to the analysis of ordinary light; this is followed by a description of the ingenious "X-ray spectrometer," devised and constructed by the authors for carrying out their investigations; then follow chapters in which the known properties of X-rays and of crystal structure are discussed. In Chapter VI. we come to the important subject of X-ray spectra; full use is made of the researches of Whiddington, Moseley, and others, and some remarkable spectrum diagrams of the X-ray bands of rhodium are shown.

The authors then turn to the analysis of crystal structure as developed by the aid of X radiation, and nearly one hundred pages are devoted to its elaboration; the section will be found of deep interest to crystallographers, and illustrates very clearly the great advance that has been made.

Chapter XI., "The Intensity of X-ray Reflection": Prof. Bragg in his preface gives the credit of the work in this section to his son, Mr. W. L. Bragg. Using the homogeneous beams produced by anti-cathodes of platinum, osmium, and rhodium, much valuable data has been obtained, but it is indicated that the work is only at its commencement. It is much to be regretted that the present upheaval of society has necessitated the cessation of the work on the part of Mr. W. L. Bragg, who is at present engaged upon quite other duties; we sincerely hope that

this abnormal condition of things will not be of long duration, and that this brilliant young physicist will soon be able to continue the work so well begun.

The final chapter is devoted to the analysis of the Laue photographs, and the researches and theories detailed in the early part of the book are brought to a focus in the interpretation of the beautifully symmetrical patterns produced by the diffraction of X-rays through various crystals and a review of the results gained by other workers in the same field.

There is a short appendix containing some supplementary notes that will be of value to future workers in this interesting branch of physics.

The authors' object has been to give a simple and brief introduction to this new field of activity, and they have done so in a manner that adds charm to an already fascinating subject.

*Science and Industrial Problems.* By Prof. ARTHUR W. CROSSLEY, D.Sc., F.R.S., For. Sec. C.S.

IN this lecture, which was delivered at the Royal Institution in February of this year, Prof. Crossley took as his theme the statement that "pure scientific research work, carried out in the laboratory, is the soul of industrial prosperity," and illustrated it by well-chosen examples from practical results recently obtained by the application of organised research to industrial problems. His explanations were clearly expressed in not unduly technical language, and the emphasis laid upon the need for the organisation of the efforts of physicist, chemist, and engineer is fully justified. The three problems chosen for discussion were the oxidation of the nitrogen of the air, hardening of fats by catalytic hydrogenation, and the preparation of different coloured derivatives of anthraquinone, and in each case the method of attacking the problem and the results obtained were described in some detail. In connection with the first problem—the utilisation of atmospheric nitrogen—it may be pointed out that Prof. Crossley is in error in stating that Lord Rayleigh in 1897 was the first to demonstrate the possibility of forming nitric acid by direct union by the agency of the electric spark. In 1892 Sir William Crookes had shown that the electric arc can be employed to make nitrogen burn in air with a powerful flame, and the suggestion that the power of water-falls could be used to effect the union upon a commercially successful scale came from the same source.

## OBITUARY.

SIR A. H. CHURCH, K.C.V.O., F.R.S., M.A., D.Sc., F.S.A. (sometime Professor of Chemistry in the Royal Academy of Arts in London).

THE news of the death of Sir Arthur Herbert Church, which occurred on Monday, May 31, at his residence at Kew Gardens, will cause deep regret to his many friends.

Sir Arthur Church was born on June 2, 1834, in London, and was educated at King's College, London, the Royal College of Chemistry, and Lincoln College, Oxford, where he took a first-class in the School of Natural Science. For sixteen years, from 1863 to 1879, he was Professor of Chemistry at the Royal Agricultural College, Cirencester, and was subsequently appointed Professor of Chemistry to the Royal Academy of Arts. He was also Lecturer in Organic Chemistry at the College of Engineering at Cooper's Hill. He was keenly interested in many branches of chemistry, and his publications covered an unusually wide range of subjects. In his early days he made a special study of agricultural chemistry, and wrote articles dealing with the analysis of plants and vegetable products,

potato disease, and the chemistry of vegetable albinism; he was the discoverer of the reddish violet amorphous pigment turacin, which is found in the feathers of birds, and he showed that it contains about 7 per cent of copper. He demonstrated the occurrence of aluminium in certain vascular cryptogams, and investigated the properties of chlorophyll and of colein or erythrophyll. He was, more over, responsible for a great number of important contributions to mineralogical chemistry, and studied the composition of many minerals, including, among others, autunite, atacamite, chalybite, zircons, and churchite, a British cerium phosphate which he discovered. He had a thorough knowledge of the minerals of Cornwall, and was the possessor of an excellent collection of precious stones. In collaboration with Sir William Crookes he published, in 1864, an important paper on thallium iron alum. His lectures at the Royal Academy on the chemistry of paints and painting contained much original matter, and went over ground which had never been adequately covered before.

His remarkable versatility may be seen from the titles of the many books of which he was the author; these invariably met with a high degree of success and ran through many editions. Thus, the ninth edition of his "Laboratory Guide," a manual of practical chemistry for agricultural students in colleges and schools, was published in 1912, and the fourth edition of the "Chemistry of Paints and Painting" has recently been noticed in the columns of the CHEMICAL NEWS. Several editions of his books on precious stones, English earthenware, and English porcelain have also been published. He edited and revised Prof. Johnson's "Chemistry of Common Life," adding greatly to the value of an already much appreciated book, and he also wrote a treatise on the food grains of India, and a manual of colour.

Sir Arthur Church held the degrees of M.A. and D.Sc. (Oxon.); he was elected a Fellow of the Royal Society in 1888, and served on the Council from 1911 to 1912. For three years he was the President of the Mineralogical Society. His artistic tastes were strongly developed, and he had been an exhibitor at the Royal Academy. He was a man of unique knowledge, and was one of the greatest authorities upon the chemistry of paints. His death is a great loss to the scientific world.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx. No. 17, April 26, 1915.

Action of Sodamide on Allyldialkylacetophenones. Preparation of 3,5-Dimethyl-3-ethyl and 3,3-Diethyl-5-methylpyrrolidones.—A. Haller and Edouard Bauer. —The action of sodamide upon allylmethylthylacetophenone and allyldiethylacetophenone is similar to that upon their lower homologue, the corresponding disubstituted methylpyrrolidones being formed. This condensation appears to be a general reaction for allyltrialkylacetophenones, and is probably generally applicable to all ketonic compounds in which there is a double bond in the  $\gamma$ -position with regard to the ketone function.

Vol. clx., No. 18, May 3, 1915.

Determination of  $\gamma$  from the Velocity of Sound.—A. Leduc.—The author has worked out the values of  $\gamma$  (the ratio of the two specific heats) for various gases and vapours, using the formula  $V = \phi \sqrt{\frac{RT}{M(1+\frac{\gamma}{2})}}$ , where  $V$  is the velocity of sound. The results obtained are by no means good, partly owing to the difficulty of obtaining the vapours in the pure state.

*Bulletin de la Société Chimique de France.*

Vol. xvii.-xviii., No. 5, 1915.

Action of Halogens upon Mercuric Sulphate. —M. Chateau.—When iodine acts upon mercuric sulphate in presence of water a crystalline product is obtained, which on analysis gives results which closely agree with those of Brückner's complex salt,  $6(3\text{HgO} \cdot 2\text{SO}_3) \cdot 6\text{HgI}_2 \cdot \text{HgI}_2\text{O}_6$ . The author believes, however, that this product is not a single salt but the result of the equilibrium of three salts, dimercuric sulphate  $6\text{SO}_4\text{Hg} \cdot \text{HgO}$ , mercury iodosulphate  $6\text{SO}_4\text{Hg} \cdot \text{HgI}_2$ , and mercury iodate  $\text{I}_2\text{O}_6\text{Hg}$ . When bromine or chlorine acts on mercuric sulphate the products are the bromide or chloride of mercury respectively.

## MISCELLANEOUS.

Royal Society.—In addition to the meeting of the Society previously announced for June 10, that for June 24 will not be held.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Lieut.-Col. A. G. Hadcock was elected a Member. The Secretary announced the decease of Sir Arthur H. Church, K.C.V.O., F.R.S., and Hugo W. Müller, Ph.D., D.Sc., F.R.S., Members of the Royal Institution, and Resolutions of Condolence with the relatives were passed.

"Neptune."—The Anglo-Belgian paper *Neptune* is a weekly journal giving shipping, motor-shipping, industrial, commercial, and financial news, and is printed partly in French and partly in English. It provides a useful advertising medium, and should do good work in helping to rebuild Belgium's trade and industries when the time comes. The Business Manager, Mr. E. V. Questier, Bank Chambers, 329, High Holborn, W.C., will be pleased to send *Neptune* free of charge for a month to any reader of the CHEMICAL NEWS who mentions the latter in his application.

## NOTES AND QUERIES.

\* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chromic Acid.—I shall esteem it a great favour if I can be informed where I can obtain chemically pure chromic acid. I would prefer dealing direct with the manufacturer, as the quantities I want would warrant it.—A. MCSWINLY.

## MEETINGS FOR THE WEEK.

THURSDAY, 17th.—Royal Society. "Analyses of Agricultural Yield—Part II., The Sowing-date Experiment with Egyptian Cotton, 1913," by W. L. Balls and F. S. Holton. "Soil Protozoa and Soil Bacteria," by E. J. Russell. "The Enhanced Series of Lines in Spectra of the Alkaline Earths," by W. M. Hicks. "Certain Linear Differential Equations of Astronomical Interest," by H. F. Baker. "The Partial Correlation Ratio," by K. Pearson. "Effect of Temperature on the Flowing of Water when Flowing through a Constricted Tube," by S. Skinner and F. Entwistle. Chemical, 8.30. "Rotatory Dispersive Power of Organic Compounds—Part VIII., Tartaric Acid and the Tartrates," by T. M. Lowry and P. C. Austin. "Study in the Coumarin Condensation," by B. B. Dey. "Formation of Heterocyclic Compounds from Hydroxymethylene Ketones and Cyanoacetamide," by H. K. Sen-Gupta. "Nitrocamphor and its Derivatives—Part VIII., Action of Formamide on Nitrocamphor," by T. M. Lowry and V. Steele. "Reactivity of the Halogens in Organic Compounds—Part VIII., Interaction of Alkaloids and Alkali Bromoacetates and Bromopropionates in Methyl Alcohol Solution and in Mixtures of Methyl Alcohol and Water," by G. Senter and H. Wood. "Properties of Cold-worked Metals—Part II., Methods of Measuring Small Changes of Density produced by Annealing," by T. M. Lowry and R. G. Parker.

# THE CHEMICAL NEWS.

VOL. CXI., No. 2899

## NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

It might be instructive and interesting if the chemical analyses of a few familiar plants were presented, the results of which, when duly considered, would lead to a closer understanding of the physiological processes of which these plants are the seat. There is no doubt that the anatomical structure and the mode of life of plants as well as their habitat react seriously on their chemical energy and productiveness. In some plants the stem (supporting organ) may be practically absent, others may be water-plants, or may grow and propagate satisfactorily only on dry sandy soils free from strong nutritive solutions, and there are others still that deposit a great amount of excreta, or exhibit a curious carnosity or a blatant and blowzy habit, the result of the influence of the environment, &c. According to Rochleder, "the relationship of plants is determined by compounds of the same chemical nature which they contain." This statement seems true qualitatively, as it were, but not quantitatively, as many plants produce tannin, for instance, which are near allies of plants which are free of it, the difference depending upon the rate of growth, the height and dimensions of the plant, the number and needs of the branches, leaves, flowers, and fruits, the greater or lesser sensitiveness of the protoplasm to the influences of the environment, &c.

*Bracken (Pteridium aquilinum).*—Best of all on half-shaded places strewn with fallen leaves on sandy soils this plummy fern flourishes with all the luxuriance incident to the vigorous development of the leaves in contrast to the stumpy almost imperceptible stem. The root (rhizome) is deeply sunk in the soil, and it is clothed only sparsely with hairs, which, however, manage to extract and elaborate certain mineral matters thereof, even though existing in quite small quantity. The fertile leaf (frond) is similar to an ordinary leaf in formation and nervation, but is distinguished by its stronger lignification, the reduction of its parenchyma, the very large air-cavities, the leathery consistence, and the continuous terminal growth. The chemistry thereof also differs, as the following analysis of the pinnæ taken at the end of July indicates. The benzene extract of the dry matter amounted to 2 per cent, and consisted mostly of wax, with very little carotin, and no fat-oil apparently. A subsequent extract with alcohol yielded about 3 per cent of an iron-greening, phlobaphenic, catechol tannin (tannoid is present only in the young frond), and a good deal of cane-sugar or levulose. In addition to these there was much pectosic mucilage and some free phlobaphene; a large quantity of reserve starch and a good deal of oxalate of calcium were yielded to hot dilute HCl; the residue (crude fibre) was about 43 per cent of the original dried leaf. The ash of the whole dried frond was 4 per cent, and yielded 30.4 per cent soluble salts, 17.3 silica, 19.3 CaO, 9.2 MgO, 10 P<sub>2</sub>O<sub>5</sub>, 5.9 SO<sub>3</sub>, 9.4 Cl, and very little Mn or carbonates. The entire overground parts of the plant at said date contained 15 per cent proteids. There was some nitrate in the fronds, and although this fern flourishes vigorously on soils copiously supplied with symbiotic fungi, none of these are found attached to its roots. The special chemical feature of ferns which distinguishes them from the lower plants is the presence of abundant lignin in their tissues, which is connected with a very efficient

process of assimilation. In the first place cellulose is produced by the protoplasm as a permanent structure which is never resorbed like starch, and hence it possesses the property of dehydrating, or drying to a certain extent. Hence, also, it becomes capable of absorbing into its molecular and chemical structure a number of colloid constituents collectively known as lignine, which are products of deassimilation for which the cellulose has a very special affinity; in addition thereto various mineral matters, lime and silica especially, are also attracted by the dehydration and lend additional support to the framework of the cell wall. The tissues of algæ, fungi, lichens, and mosses never produce lignine, presumably because their cell walls decompose into pecun, or form chitin probably by hydration, or the sap which bathes them is free from adsorbing colloids. Very vigorous when young the vitality of the bracken rapidly wanes; the protoplasm rapidly discharges its chemical activity, the proteids solubilise and diminish (only 4.4 per cent in autumn), the external tissues dry up, and silica creeps therein extensively (the ash has now 53 per cent SiO<sub>2</sub>), and about October 1 its rich greenery has passed to bright yellow at the foot of the mountains, melting gradually through orange to a dark russet-brown towards the high windy and rocky summits.

*Pink Campion (Lychnis dioica).*—This plant flourishes on cold clay in woods, damp hedge-banks, and on stream-side rocks. The leafy shoots and the erect fertile stems proceed from the root system itself, and are not highly differentiated, only the pericycle of the stem being very developed and lignified. On June 21 the dried leaves yielded 2 per cent carotin and wax; the alcoholic extract contained no tannoid, tannin, or sugar, but only a kind of saponin not precipitated by acetate of lead or baryta water, and seemingly similar in reaction to the scullian of squill; further treatment yielded considerable mucilage and nitrate, much reserve starch, and oxalate of calcium (localised especially in the cells immediately below the palisade tissue). The ash of the dry leaf amounted to 16.6 per cent, and contained 50.7 per cent soluble salts, 4.3 silica, 17 lime, 5.2 magnesia, 3.8 P<sub>2</sub>O<sub>5</sub>, 2.5 SO<sub>3</sub>, and 6 Cl; there was very little manganese, and the carbonates were nearly all soluble. There was much chlorophyll, although true chloroplasts are very scanty; in fact, this plant is a powerful producer of starch, carotin, chlorophyll, and oxalate of calcium which is deposited in all the organs. Later on, on August 19, an aqueous extract of the overground parts of the plant contained considerable nitrate and much cane-sugar; there were evidences of a tannin which reacted like caffeotannin, and also of a phloroglucide, both in small quantity; some decomposition products appearing of a saponin quinonic character seemed to be predominant, probably arising from the oxidation of a tannoid. According to Russel this plant has glucosides only in its young shoots near the vegetative tip, and only traces thereof in the old stem; a fact which indicates decomposition with production of saponin or alkaloid, possibly choline in this case. A very notable feature of the plant is the brilliant conspicuity of its flowers, the calyx being a deep dull red or reddish purple, while the corolla is deep uniform purplish rose. It is observed that most of the leaves are collected near the roots, only a very few small sessile leaves appear on the long stem, and the uppermost of these is not near the flowers. Hence, therefore, it is natural that the nitrogen required by the reproductive organs at the flowering and fruiting periods should be obtained to a great extent from the corolla as well as from the leaves, which latter cannot alone afford enough of that indispensable element. The drain on the corolla induces a special activity of deassimilation therein, and in this way we account for the eminent power of colour possessed by corollas in plants which, like the campion, produce a vast quantity of acid and very little tannin. The fact also that in this case the calyx is also tinted red shows that in an organ, which in most other cases is green and assimilatory, a special activity of



deassimilation is occasionally a physiological necessity. In many plants the stem or the leaf also participates in the display of pigmentation in places normally green or brown, and for a precisely similar reason. In fact, wherever in the organs of a plant the phenomena of heightened vitality occur from natural or artificial causes, there is a rush of nitrogen to the part affected with an increased intensity of respiration, and hence therefore a high level of deassimilation in other parts or organs, leading to the production of coloured pigments in lieu of the ordinary colourless tannins.

*St. John's Wort (Hypericum perforatum).*—The analysis of this plant is well worthy of being presented, inasmuch as its anatomical structure and certain of its organic constituents indicate very clearly that it is not to the manner born here, and that it hales rather from nearer the tropics as its native seat and origin. Its stem is highly differentiated, and is of three kinds according as it arises from seeds, root-buds, or the base of old stems. On August 5 the dried overground parts yielded to boiling benzene 1.2 per cent of mostly wax with a little carotin and fat oil; the alcoholic extract contained much flavone yielding fine orange lakes with Al and Sn salts, and alkaline earths, a fine yellow compound with HCl, and seemed to be similar to the gossypetin of the Malvaceæ; there was also a little phlobaphenic catechol tannin with reactions similar to tea tannin, and much resin. There was no nitrate, reserve starch, or oxalate of calcium; hence this plant is nourished partly by mycorrhiza (root-fungi), the root system is faintly developed, and its nitrogen is got from organic compounds in stations poor in nutriment salts. The rigidity of the stems is due to a high percentage of dry matter, and hence the mucilage is mostly extracted by dilute soda and not by hot water alone. According to D'Arbaumont the chlorophyll of the leaf occurs in detached flakes and not in true chloroplasts, and there is no starch therein between April and September. The ash yielded 38.1 per cent soluble salts, 7.9 silica and sand, 15.2 lime, 7.4 magnesia, 12.1  $P_2O_5$ , 6.5  $SO_3$ , 5.5 Cl, with a good deal of iron and manganese, but very little  $CO_2$ . The chemistry of this plant indicates that it is a lover of dry air, which tends to increase the secretory canals and secretions. Assimilation is not intense, and deassimilation does not work up acids, but only copious quantities of resin, tannin, pigment, and volatile oil. The peculiarity seems to be that this plant seems to find within its internal anatomy, as it were, sufficient room for the accommodation of its excreta. The numerous secretory sacs in the leaf blade which appear as so many black or pellucid holes or dots do not reach the epidermises, they only occupy nearly all the space between them. There is, however, a careful isolation of these receptacles from the general thin-walled cavity where the gases and vapours incident to the vital processes circulate before reaching the stomata.

*Water Lily (Nymphaea alba).*—This plant is specially interesting owing to the circumstance that its chemistry is intimately connected with its anatomy and physiology. Slow rivers, lakes, and clear ditches are its habitats on a peaty bottom; i.e., a soil with much nitrogen which is a kind of protein and acid ulmin (not humus) deficient in mineral plant food, and bad for the supply of air and nitrate. A special feature of the anatomy is the comparatively small development of the body of the plant, there being no stem, only a thick fleshy rhizome which emits a great number of long spongy roots, a rapid succession of petioles, and a certain number of floral peduncles; all these are provided with vascular bundles which are remarkable for the extreme reduction of their xylem (conducting) portion. On the other hand, these organs are copiously provided with large air-canals and lacunæ which penetrate the whole of the tissues and freely supply oxygen thereto. The rhizome extracted by boiling benzene yielded about 4 per cent of fat and resin, with some alkaloidal matter dissolving in  $H_2SO_4$  with a deep red-brown colour passing to a fine grass-green. The alcoholic

extract was mainly of tannin, which gave no HCl-vanillin or pine wood reactions, and responded to all the tests for gallotannin; it seemed readily oxidised to gallic and ellagic acids by boiling with dilute  $H_2SO_4$ , and by various oxidising agents. Further, the presence of sugar was doubtful, but there was much mucilage which was not pectosic apparently, and a great accumulation of oxalate of calcium and of reserve starch not readily convertible into glucose; there was also evidence of a combination of tannin with the lignin of the vascular bundles and perhaps also with the cutin of the epidermis. The leaves were easily dried and powdered, and on boiling with benzene yielded a large quantity of carotin, wax, and fat, with much phytosterol. The alcoholic extract had some resin and much gallotannin, same as in the rhizome; there was also a tannoid yielding paracarthamin, and also vivid yellows with Al, Sn, and Pb salts, and by aceto-HCl. Further treatment of the residue of the leaves yielded no nitrate, a moderate amount of glucose and cane-sugar, very much pectosic mucilage, much reserve starch, and oxalate of calcium, but no free phlobaphene. The ash of the dried leaves amounted to 11.07 per cent, and contained 55.3 per cent soluble salts, 3.8 silica, 15.9 CaO, 2.7 MgO, 5.15  $P_2O_5$ , 13.5 Cl, 2.2  $SO_3$ , and about 5 oxides of Fe and Mn; there was a little soluble phosphate and about 20 per cent  $CO_2$ . This analysis indicates a poverty of nitrogenous matters, but a great power of reserving or storing up the products of assimilation (starch and fat-oil), while at the same time the products of deassimilation (tannins and acids) are highly oxidised. It would seem that the acid humus of the peaty bottom makes it unnecessary for the roots to have much oxygen in aid of their absorptive activity, while the poverty of nitrogen in the plant is helpful to the oxidative influences of the medium. Peroxydases, manganese compounds, katalases, &c., have been mentioned as agencies in this connection, but in view of the diffusion of air and water canals in the tissues these hypothetical assumptions are quite unnecessary. This plant has been placed in the monocotyledons by Richard, Lyon, and others; it is nearly related to *Hydrocharis*, *Alisma*, *Butomus*, and *Triglochin*, and judging by the colour of the flowers of some of these they also produce gallotannin. The production of this highly oxidised tannin in well aerated water-plants connected by systematic morphological characters with land-plants in which it is unknown, seems to prove that the chemistry of any particular species, so far at least as the process of deassimilation is concerned, is entirely dependent on its mode of life and habitat. If the medium in which it lives is specially oxidative its constituents will be more or less oxidised, and even, as is the case with the tannin of the water-lily, be capable of some further oxidation under favourable conditions by natural or artificial agencies. In this plant the conditions of tannic deassimilation seem to be absolutely natural and normal; that is, they are not attendant upon any pathological phenomena. An important feature in this connection is that the floral peduncle arises from the rhizome entirely independently of any leaf axil, and there is no visible trace of a bract; this means that the floral organs are nourished entirely and directly by the roots and are not aided in any way by the leaves. The consequence of this provision is that there is a double drain, as it were, upon the roots as respects soluble nitrogen, carbohydrates, and salts, the result being that this organ is the seat of an intense deassimilation with the production of a large quantity of gallotannin absolutely free from any trace of catechol tannin. So that what in other vegetable organs would represent pathological phenomena are in the water-lily strictly the natural consequences of normal physiological processes. The red variety of the flower found in Sweden indicates that there is an insufficiency of nitrogenous food for local reasons supplied to the stamens, and hence they are obliged to draw specially upon the proteids of the corolla, which solubilise, deassimilate, and produce anthocyan.

Patterdale, Westmoreland.

# THE CHEMICAL INDUSTRIES OF GERMANY.\*

By Prof. PERCY F. FRANKLAND, F.R.S.

(Concluded from p. 280).

THE facts which I have brought forward speak for themselves, and proclaim in the most convincing manner the stupendous progress which has been made by Germany in the chemical industries during the past forty years. It is equally certain that England, once pre-eminent for chemical manufactures, has not progressed at the same rate, and is at the present moment suffering much inconvenience through being so largely dependent on German chemical products of one kind and another. The country is now reaping the harvest of humiliation which it has sown for itself in spite of the warnings repeated *ad nauseam* by the chemical profession during a whole generation. The systematic neglect of chemical science and the failure by manufacturers to utilise the services of highly qualified chemists, could only lead to the result that all the industries which are dependent on a profound knowledge of chemistry should tend to disappear from our midst and pass into the hands of those who are prepared, not only to apply new chemical discoveries to industry, but even to prosecute the most varied chemical investigations in the hope of sooner or later making discoveries which shall be of advantage to their commercial undertakings. The mischief caused through the neglect of chemistry by practical men in this country has been so subtle that to a large extent it has remained concealed from the average man of intelligence and from the governmental classes. During the past forty years our country has been accumulating wealth in an altogether unprecedented fashion, so that the loss or restriction of some industries appeared a matter of unimportance to political observers taking only a broad and superficial survey of the national resources. The whole of our arrangements have evolved during the past half-century on the assumption that this country would never again be engaged in a European war, whilst still more recently the new democracy has vainly boasted that it could prevent such a war by means of a general strike. The year 1914 has seen the dissolution of many fool's paradises and has given the *coup de grace* to all these vain imaginings, with the result that we find our vast textile industry in serious peril because the much smaller dyestuff industry has been complacently allowed to slide into the hands of our sagacious and more painstaking enemies. The same carelessness and want of foresight had even allowed us to become dependent on Germany for some of the most important materials used as explosives, e.g., trinitrotoluene, and for many of the most valued drugs required alike by our army, navy, and civil population.

The complete breakdown in our supply of fine chemicals, which is the direct outcome of the disregard of the constant warnings emitted by scores of British chemists, has led the Government of the day to intervene and attempt to remedy the intolerable state of affairs which has arisen in connection with the supply of coal-tar colours.

We devoutly hope that success will attend the endeavour to establish the coal-tar colour industry in these islands on the largest possible scale. Whatever the ultimate scheme adopted may be, I would venture to point out that it must be based on a clear understanding of the following considerations:—1. That the provision of the required chemicals during the continuance of the war is one thing, and that their production on a commercial basis after the cessation of hostilities is quite another matter. 2. It appears to me that in order to provide the needful supply during the war the only reasonable course is to assist in every possible way those firms which are already making similar or closely allied products, so as to enable them to produce their present goods on a larger scale, and

as far as practicable to undertake the manufacture of others which are urgently required. The immediate problem will be also greatly facilitated by utilising supplies obtainable from neutral Powers, and more especially from Switzerland, which is the only country, other than Germany, in which the manufacture of dyestuffs and similar chemical products has been vigorously prosecuted. As a matter of fact Mr. Runciman admitted in the House a short time ago that the Government had granted licences to trade with the enemy in the matter of dyestuffs! 3. As regards the prospects of the home industry after the war it will require "nursing." I use the term advisedly, in order to obviate the employment of another and much more familiar one, which is so dear to some politicians and so hated by others; it will require nursing for a much longer period of time than has hitherto been mentioned. In this connection I would point out that the sum of £10,000 a year for ten years, which it has been proposed to guarantee for research purposes, is absurdly inadequate. 4. If the industry is to prosper it will not only have to manufacture materials already known, but also continually to be introducing new products of its own discovery, as well as constantly to be seeking to produce more economically a great number of auxiliary chemicals required in the manufacturing processes. It is also essential that the undertaking should branch out into the manufacture of other materials as occasion may arise for advantageously utilising by-products. 5. The competition which the industry will have to suffer from Germany is likely to be much more serious than is generally supposed, because it must be remembered that England only takes, as we have seen, about one-fifth of the total German exports of dyestuffs, so that it would be comparatively easy for German firms specially to reduce the price of the goods sent to England. They have already done this in America when attempts have been made to start an aniline industry there. It is particularly significant, and augurs ill for the prospects of this scheme to rehabilitate the coal-tar colour industry, that the latter has failed to flourish anywhere excepting on German soil, and that countries with fiscal systems entirely different from our own have been no more successful in this respect than have we ourselves. 6. It will certainly be necessary that expert chemical knowledge should in the future be much more highly remunerated than it has been in the past, otherwise the supply of able and properly qualified men will not be forthcoming. The flow of men of high-grade intelligence into a profession is determined by the prizes which the profession has to offer, in the form of money and social position. Consider the great stream of able men who are attracted to the English Bar, in which profession the prizes, although limited in number, are of the most substantial kind, with the result that the successful leaders are selected by the fiercest competition in a very wide field. If there is to be a large influx of high intelligence into the chemical profession it will be necessary that there should be some very different prizes from the paltry bait which is offered at the present time, for the study of chemistry in this country now only draws those men who either have or think they have an overpowering zeal and passion for the science, to which they devote themselves against the advice of their friends and in spite of the warnings of the professors of chemistry by whom they are initiated. Notwithstanding the absence of material inducements, I venture to say without fear of contradiction that there is more original investigation being prosecuted in this country by chemists than by any other body of British men of science, and this I attribute to the fact that such a large proportion of our number have either been at German Universities or are the pupils of those who have been at these centres of research. Nor are any of us, I am sure, even during this unfortunate crisis, unmindful of the hospitality and the inspiration which we have received in the schools of the enemy. 7. If the proposed undertaking is to succeed real chemists must be on the directorate, and in a sufficient proportion to

\* Meeting held at Birmingham University on March 4, 1915. From the *Journal of the Society of Chemical Industry*, xxxiv., No. 7.

give effect to their views. Many men of science are excellent business men. What does experience teach in the case of flourishing chemical industries which we fortunately still have amongst us? What does not the firm of Messrs. Brunner, Mond, and Co., for example, owe to the late Dr. Ludwig Mond, F.R.S.? 8. In attempting to establish a commercially successful coal-tar colour company on a large scale in this country, I venture to think that the Government have undertaken a task which they will find to be surrounded with difficulties of quite a different order from those which they have had to encounter in some of their most striking previous legislative acts, such as the provision of salaries for members of Parliament, the granting of old age pensions, and the establishment of a compulsory system of insurance. These are matters in which if the Government dictate we are obliged to obey, but the commercial success of an industry which is based upon progressive scientific investigation depends upon factors so subtle and elusive that they cannot be coerced even by a majority of the House of Commons. 9. If the chemical industries are to be rehabilitated in this country there must be a complete change in the attitude of mind towards science in general and towards chemical science in particular amongst the influential classes of the population, and it will certainly not be effected by following the precept "Business as Usual," but by pursuing a policy which is the exact opposite of what is implied by that vulgar and undignified phrase.

#### THE COMPOSITION OF TYPES OF SOME CHEMICAL GLASSWARE.

By F. W. BRANSON, F.I.C.

THE problems arising out of the present war as regards the supply of chemical glassware very soon became acute, owing to the fact that practically the whole of the glass apparatus used in this country was obtained from Continental sources, chiefly Germany and Austria. I therefore took early steps to ascertain by means of chemical analyses the composition of typical chemical glassware in general use, more particularly beakers and flasks and miner's lamp glasses. The composition of these having been ascertained, it was possible to give manufacturers working formulae in October last. In order to secure economy and facility of output, one glass, a zinc borosilicate, was selected for the manufacture of beakers and flasks, which were by that time urgently needed, by ordnance works more especially. This glass has been adopted by the British Laboratory Ware Association, Limited, as exhaustive tests have proved it to be similar to what was the best obtainable previously, namely, Jena "zinc borosilicate" glass. Reports on "B.L.W." glass from various expert and other sources, particularly from ordnance works, prove it to be, if carefully annealed, a reliable and economical substitute for the various types of chemical glassware previously in use. A 750 cc. flask, made from an early batch, was reported on as follows on December 14, 1914:—"About 250 cc. of water was put in the flask and well boiled, then quickly cooled by holding under the tap. The water was boiled again and quickly poured out, and cold water run into the flask whilst as hot as possible. About 10 grms. of drillings was dissolved in hydrochloric acid, evaporated to dryness, baked hard, cooled, and dissolved in hydrochloric acid. This was repeated three times. In the last case baking was continued for  $1\frac{1}{2}$  hours, on the hottest plate. 300 cc. of 20 per cent caustic soda solution was put in the flask and kept at a steady boil for two hours. The soda was quickly poured out and the flask plunged under cold water. There was no indication of 'frosting' on drying the flask."

The constituents of a large number of glasses will be found in Thorpe's "Dictionary of Applied Chemistry," ii., 719; also in "Formulas for Glass Manufacture" by the Institute of Chemistry (*Journ. Soc. Chem. Ind.*,

1915, April 30, 424); and in "Notes on Glass," by the National Physical Laboratory (*Ibid.*, 1915, March 15, 210).

The work I have carried out is partly covered by the "Notes on Glass" and "Formulas for Glass Manufacture" alluded to above; therefore I have not given any analytical data of glasses for which analyses have been recently published except in the case of Kavalier's potash-soda glass, which show the close similarity between the two analyses, the figures in the second column being those given in "Notes on Glass."

	Per cent	Per cent.
SiO <sub>2</sub> .. .. .	75.96	76.02
Al <sub>2</sub> O <sub>3</sub> .. .. .	0.40	0.64
Fe <sub>2</sub> O <sub>3</sub> .. .. .	0.08	trace
CaO .. .. .	8.48	7.38
MgO .. .. .	0.14	0.30
K <sub>2</sub> O .. .. .	7.48	7.70
Na <sub>2</sub> O .. .. .	7.34	7.60
	99.88	99.64

This glassware was found to be next in order of merit to the Jena zinc boro silicate glass, but owing to the war the supplies of potassium salts practically failed, therefore this type of glass was not recommended for manufacture. Experiments were also made, and are being continued, with a hard soda glass, which works well in the blowpipe flame, the analysis being as follows:—SiO<sub>2</sub>, 76.18 per cent; Al<sub>2</sub>O<sub>3</sub>, 2.86; Fe<sub>2</sub>O<sub>3</sub>, 0.07; CaO, 4.52; MgO, 0.14; Na<sub>2</sub>O, 16.43 per cent.

No analyses were made of soft soda glasses, as these were already obtainable of British manufacture for the production of test-tubes, &c.

Analyses were also made of two distinct types of glass combustion tubing. A Jena sample contained SiO<sub>2</sub>, 66.40 per cent; Al<sub>2</sub>O<sub>3</sub>, 6.38; Fe<sub>2</sub>O<sub>3</sub>, 0.22; BaO, 7.27; CaO, 7.94; MgO, 0.61; K<sub>2</sub>O, 2.40; Na<sub>2</sub>O, 1.25; B<sub>2</sub>O<sub>3</sub>, 7.22 per cent.

The other type of combustion tubing (Kavalier) gave the following figures:—SiO<sub>2</sub>, 79.57 per cent; Al<sub>2</sub>O<sub>3</sub>, 0.32; Fe<sub>2</sub>O<sub>3</sub>, 0.038; CaO, 7.80; MgO, 0.11; K<sub>2</sub>O, 11.60; Na<sub>2</sub>O, 0.66 per cent. The infusibility of this glass is due to the high percentage of silica present.

A further problem investigated was the miner's lamp glass, the Continental supply having practically ceased. So far as my knowledge goes, the Jena miner's lamp glass was the best then in use, and the analysis of one specimen gave the following:—SiO<sub>2</sub>, 73.08 per cent; Al<sub>2</sub>O<sub>3</sub>, 1.98; Fe<sub>2</sub>O<sub>3</sub>, 0.15; CaO and MgO, traces; Na<sub>2</sub>O, 7.76; B<sub>2</sub>O<sub>3</sub>, 17.22 per cent.

With instructions as to procedure these figures were given to a manufacturer, but the glass was found difficult to work, being rather pasty, even at a high temperature. The working formula was then altered, with much better results, and the lamp glasses will bear the Board of Trade test of immersing in cold water and raising to boiling-point, continuing at that temperature for twenty minutes, then suddenly plunging the glass into cold water (temperature 15° C.); no fracture resulted. It is a very tough glass, and is broken with difficulty, say by a miner's pick.

The sand used in my experiments was of French origin and almost entirely free from iron. The calcium carbonate and aluminium hydroxide were of British origin and were commercially pure.

The high temperature coke furnace I used for the experiments was a very convenient one for the purpose, as the temperature could be readily regulated up to white heat, and each experiment could be carried out in duplicate under the same conditions, similar to those obtaining in glass works. Each melt could be started cold and continued at the desired temperature for many hours.

In conclusion, I beg to express my indebtedness for analytical and other assistance to Mr. F. H. Branson and Mr. W. McD. Mackey.—*Journal of the Society of Chemical Industry*, xxxiv., No. 9.

THE REDUCTION OF IRON OXIDES  
BY PLATINUM, WITH A NOTE ON THE  
MAGNETIC SUSCEPTIBILITY OF IRON-BEARING  
PLATINUM.\*

By R. B. SOSMAN and J. C. HOSTETTER,  
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IN the course of an investigation on the dissociation pressures and melting temperatures of the oxides of iron we have repeatedly observed that the platinum crucibles used gained in weight and became stiff, evidently through the absorption of iron from the charges.

*Proof of the Reduction of Magnetite.*—The following experiment demonstrates the absorption of iron from magnetite by platinum under a very low oxygen pressure. About 1 grm. of natural crystalline magnetite from Mineville, N.Y., was heated to 500° in a new platinum crucible (Heraeus "extra rein," dimensions 18 mm. high, 8–10 mm. diameter) in a platinum-rhodium tube vacuum furnace and then cooled (*Journ. Washington Acad. Sci.*, 1915, v., 277). A small amount of gas was given off and was not reabsorbed. This gas produced a pressure of 0.045 mm. in a volume of 1300 cc., and was probably nearly all gas "adsorbed" by the magnetite. This gas was pumped out, and the charge then heated to various temperatures between 600° and 1200°. The temperatures were measured by a platinum-platinrhodium thermo-element and potentiometer, and the pressures were read on a 500 cc. McLeod gauge. A condensed record of the first series of heatings is given in Table I. The furnace was then cooled and the residual gas pumped out. The charge was again heated, as recorded in the second part of Table I. The results are shown graphically in Fig. 1.

TABLE I.

Temperature Deg.	Time held at t. Min.	Initial pressure. Mm.	Final pressure. Mm.
<i>First Series.</i>			
22.5	—	0.00016	—
600	18	0.0112	0.0148 (a)
1000	20	0.0510	0.0562 (b)
1200	23	0.0665	0.0776 (b)
23	—	—	0.0744
<i>Second Series.</i>			
21.0	—	0.00012	—
600	26	0.0111	0.0164 (b)
1000	16	0.0171	0.0216 (b)
1200	18	0.0236	0.0344 (b)
1000	18	0.0350	0.0360 (c)
600	19	0.0350	0.0352 (d)
1200	12	0.0396	0.0447 (b)
600	11	0.0429	0.0426 (d)
21	—	—	0.0398

- (a) Rising at decreasing rate. (b) Rising steadily.  
(c) Nearly constant. (d) Constant.

It is evident from the figures of Table I. that a reaction is going on at 1000° and higher which is supplying gas at a fairly steady rate, and that this rate is greater the higher the temperature. The changes in weight of charge and crucible, given in Table II., indicate that this reaction consists in the liberation of oxygen and the solution of metallic iron in the platinum. When heated in air after cleaning, the crucible showed on the inside the characteristic reddish black colour which appears on heating platinum contaminated with iron.

It is also evident that a small amount of gas absorption takes place as the temperature is lowered, since the pressure decreases more than can be accounted for by the

cooling of the furnace tube, but that there is no approach to a complete re-absorption of the oxygen. This decrease of pressure on cooling probably represents the re-oxidation of a small amount of dissociated magnetite; the dissociation product is as yet unknown. No metallic iron was found in the charge either by solution in hydrochloric acid, which yields bubbles of hydrogen if metallic iron is present, or by the more sensitive copper sulphate test under the microscope.

TABLE II.

	Initial weight. Mgrms.	Final weight. Mgrms.	Change in Weight. Mgrms.
Charge and crucible	4265.8	4264.7	-1.1 (loss)
Crucible alone	3261.4	3263.2	+1.8 (gain)
Charge alone	1004.4	1001.5	-2.9 (loss)

The gain in weight of the crucible, shown in Table II., has been caused partly by the absorption of metallic iron from the oxide and partly by the absorption of rhodium and also platinum from the furnace. The amount of iron absorbed, as calculated from the amount of oxygen evolved and remaining in the apparatus after cooling to room temperature, making no allowance for any permanent thermal dissociation of the magnetite, is found to be 0.9 mgrm. This is one-half of the total gain in weight.

(NOTE.—The analysis of the crucibles shows that the combined weight of rhodium and iron is less than the total gain in weight. No appreciable amounts of other metals seem likely to be present, nor were any found by the analysis. Heating a part of crucible No. 1 in hydrogen for an hour at about 600° produced no measurable loss of weight, showing that no oxide of platinum or iron is present. Some platinum must therefore have been carried from the furnace tube to the crucible, either on account of a temperature gradient between furnace and crucible or by some disintegrating effect due to the current, or by both causes combined.)

Magnetite is also reduced by platinum at high temperatures in the open air. 6.608 grms. of Merck's reagent  $\text{Fe}_2\text{O}_3$  was heated to a maximum of 1612° in an open platinum crucible (No. 509) in a 25 mm. vertical-tube platinum wire furnace. The charge melted down at about 1582°, yielding black crystalline "magnetite" on cooling. The crucible, which originally weighed 9517.3 mgrms., increased in weight to 9521.2 mgrms., a gain of 3.9 mgrms. Certain points on the bottom of the crucible attracted a light magnetic needle.

*Reduction of Ferric Oxide.*—Products containing more ferric oxide than magnetite, as well as magnetite itself, seem to be reduced by platinum under a low pressure of oxygen. This action is evident even in products which are practically pure  $\text{Fe}_2\text{O}_3$ . One crucible (No. 2) used in our work on the system  $\text{Fe}_2\text{O}_3$ — $\text{Fe}_3\text{O}_4$ , after eighteen series of measurements, had increased in weight from 2851.8 mgrms. to 2863.0 mgrms., a gain of 11.2 mgrms., or 0.39 per cent. About one-fourth of this gain is found to be due to iron absorbed. At the close of the measurements this crucible showed the usual iron coloration, produced by cleaning and heating for a few minutes in a flame. Various points on the crucible also attracted a light magnetic needle.

Under 10.2 mm. oxygen pressure at 1200°, under which conditions the magnetite is nearly completely oxidised to  $\text{Fe}_2\text{O}_3$ , this crucible gained 1.6 mgrm. Another similar crucible containing  $\text{Fe}_2\text{O}_3$  gained 1.0 mgrm. under 18.3 mm. oxygen pressure at 1200°. A part at least of these gains must be due to absorbed iron. In order to establish definitely the presence of iron in the crucibles and to determine its amount, we have made both chemical analyses and magnetic tests on the crucibles in question.

*Methods of Analysis.*—For the analysis of one portion of crucible No. 2 the platinum metals were separated from the iron by precipitating the former with hydrogen in sulphuric acid solution. (For the details of this method and for many helpful suggestions we are indebted to Dr.

\* From the *Journal of the Washington Academy of Sciences*, v., No. 9.

E. T. Allen, of this Laboratory). For the other portion of crucible No. 2 and for crucible No. 1 the method of Mylius and Mazzucchelli, by which all metals present could be determined, was employed (*Zett. Anorg. Chem.*, 1914, lxxxix., 1). In addition to iron, this method showed the presence of rhodium in both crucibles, and this latter metal was also determined. The order of agreement between the two methods for iron is shown in Table III., in which the results of the analyses are given. To test the determination of iron by the method of Mylius and Mazzucchelli, a solution containing 977 mgrms. platinum and 5 mgrms. iron was subjected to analysis; 4.83 mgrms. iron was recovered.

TABLE III.

Method of Analysis.	Crucible No.	Rhodium.		Iron.	
		Per cent.	Amount in crucible. Mgrms.	Per cent.	Amount in crucible. Mgrms.
Mylius and Mazzucchelli	1	0.077	2.40	0.158	4.90
	2	0.127	3.62	0.098	2.80
Hydrogen precipitation .. ..	2	—	—	0.085	—

**Magnetic Properties of Iron-bearing Platinum.**—The apparatus for the magnetic tests was suggested by Dr. C. W. Burrows, of the Bureau of Standards, to whom we are greatly indebted for advice and information in connection with these tests. The procedure consists essentially in weighing the pull exerted on the specimen by a strong electro-magnet. In paramagnetic and diamagnetic bodies the force is practically independent of the shape of the specimen.

Since we wished to obtain only comparative figures we did not attempt to determine the field strength or field gradient. With our apparatus as set up, 870.2 mgrms. of ferrous ammonium sulphate gave a pull of 1.74 mgrm., equivalent to 2.00 mgrm. per grm. The pull can be determined to about 0.02 mgrm. by the method of swings. The mean of two sets taken with reversal of the current eliminates a small correction due to the steel parts of the balance.

One-half of crucible No. 2 had already been dissolved for analysis. The other half was tested magnetically, and gave a pull of 0.20 mgrm. This was so much smaller than the effect which we expected on the basis of preliminary results obtained by Burrows and Burgess at the Bureau of Standards that we experimented further on the magnetic effects produced by known percentages of iron added to pure platinum. For this purpose a new 10 by 18 mm. platinum crucible (Heraeus "extra rein" was first tested, and found to give no measurable magnetic pull. Iron was deposited in the crucible electrolytically from oxalate solution, and it was then heated in the vacuum furnace, first at 1200°, later at 1400°, in order to dissolve the iron in the platinum. The results are recorded in Table IV.

Nearly twice as much iron was deposited in the same way in a similar crucible, which was similarly treated and tested. In this case the iron was deposited chiefly on the inside of the crucible, near the bottom, whereas the iron of Table IV. was distributed uniformly over inside and outside. The results of the second test are given in Table V.

Fig. 2 shows that the magnetic effect is very nearly proportional to the weight of the deposit of iron before heating has driven it into the platinum. (The first point of the curve represents a preliminary plating of crucible No. 3).

The immediate drop in the magnetic effect as soon as the iron diffuses into the platinum is very evident from Tables IV. and V., and from Fig. 3, which represents graphically the data of Table V. The surprising part of the result is that practically the same ultimate magnetic pull is attained, although one crucible contains nearly twice as much iron as the other. Furthermore, the iron

of Table V. is concentrated in a smaller area of platinum surface than that of Table IV., which might be expected to make its magnetic effect more than proportional to the amount of iron, instead of which it is found to be independent of the amount. The position of the dissolved iron in the magnetic field is without any important effect, since turning the crucible upside down makes only a few hundredths mgrm. difference in the final magnetic pull.

The summarised figures, showing the amounts of iron in the various crucibles referred to, and their magnetic effects, are given in Table VI.

TABLE IV.

Treatment	Total weight. Mgrms.	Weight of Iron in crucible. Magnetic pull.	
		Mgrms.	Mgrms.
Crucible tested alone .. ..	3125.2	—	—
Iron deposited electrolytically	3153.2	27.4	543.0 (a)
Heated at 1200° and 1.001 mm. for 8 min. .. ..	3152.6	27.4	35.5 (b)
Heated at 1200° and 0.0005 mm. for 30 min. .. ..	3152.5	27.4	23.8 (b)
Boiled in HCl, ignited 1 min. in Bunsen flame, oxide dissolved off in HCl .. ..	3151.4	26.3	25.2 (c)
Ignited in blast lamp, oxide dissolved off in HCl .. ..	3149.2	24.1	9.6
Heated at 1400° and 0.0002 mm. for 8 min. .. ..	3149.3	24.1	1.56
Heated at 1400° and 0.0007 mm. for 11 min. .. ..	3149.7 (d)	24.1	1.49

(a) Deposit weighs 28.0 mgrms., but contains some hydrogen, carbon, and moisture; (b) film of iron still on surface; (c) film removed; (d) the crucible stuck to the furnace tube—the gain in weight is probably due to rhodium absorbed.

TABLE V.

Treatment.	Total weight. Mgrms.	Weight of Iron in crucible. Magnetic pull.	
		Mgrms.	Mgrms.
Crucible tested alone .. ..	3235.6	—	—
Iron deposited electrolytically	3285.9	44.8	1110.0 (a)
Heated at 1400° and 0.001 mm. for 5 min. .. ..	3280.4	44.8	80.0 (b)
Heated at 1400° and 0.001 mm. for 5 min. .. ..	3280.3	44.7	60.0 (c)
Cleaned in HCl, dried .. ..	3278.8	43.2	54.0 (d)
Heated at 1400 and 0.001 mm. for 10 min. .. ..	3279.2	43.2	2.56
Heated at 1400° and 0.0005 mm. for 10 min. .. ..	3279.5 (e)	43.2	1.57 (f)
Heated at 1400 and 0.0007 mm. for 10 min. .. ..	3279.6 (e)	43.2	1.46 (f)

(a) Deposit weighs 50.3 mgrms., but contains hydrogen, carbon, and moisture; (b) unabsorbed iron near bottom; (c) thin unabsorbed film remains; (d) film removed; (e) the crucible stuck to the furnace tube—the gain in weight is probably due to rhodium absorbed; (f) crucible stuck to furnace tube.

TABLE VI.

	Total Weight Mgrms.	Weight of iron Mgrms.	P.c. iron.	Magnetic pull. Mgrms.
Ferrous ammonium sulphate .. ..	870.2	124.0	14.25	1.74
Crucible No. 509 .. ..	9521.2	3.9	0.04	0.74
Crucible—		(or less)		
No. 1, used in vacuo	3098.4	4.90	0.158	0.40
No. 2, " "	2863.0	2.80	0.098	0.39
No. 3 (Table V.) ..	3279.6	43.2	1.32	1.46
No. 4 (Table IV.) ..	3149.7	24.1	0.76	1.49



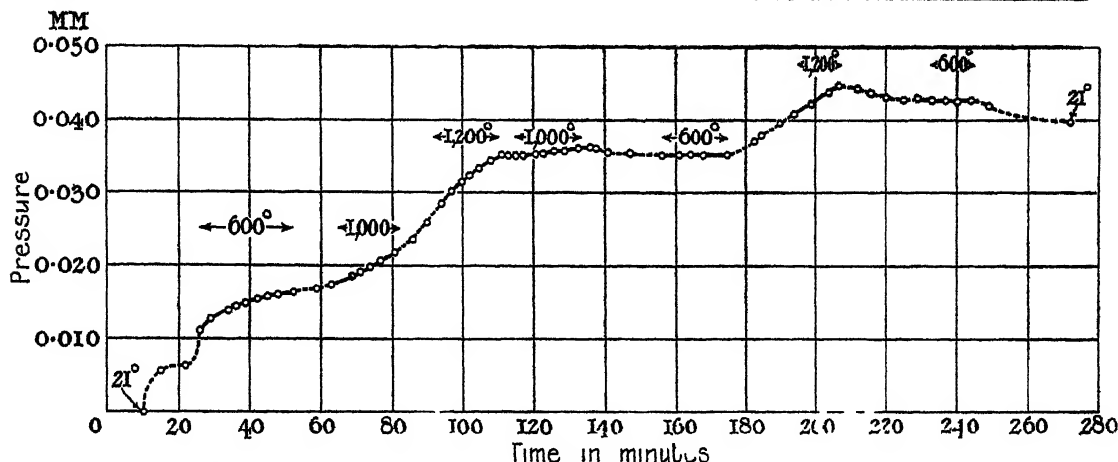


FIG. 1.—Evolution of Oxygen from Magnetite Heated in Platinum (see Table I)

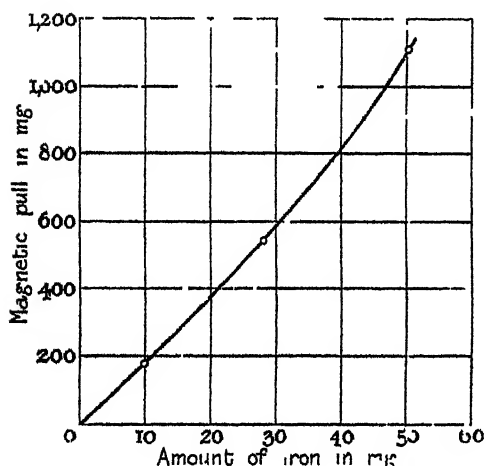


FIG. 2.—Relation of Magnetic Pull to Weight of Unabsorbed Iron.

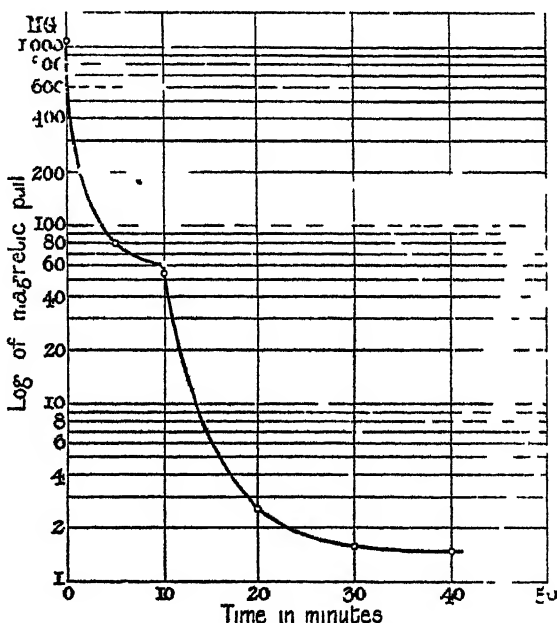


FIG. 3.—Relation of Magnetic Pull to Time of Heating Iron-plated Platinum at 1400° (see Table V).

It is evident from Table VI. that the magnetic pull must depend not only upon the amount of iron present, but also upon other factors—perhaps its concentration, distribution in the platinum, heat treatment, impurities, or other variables. As we were not prepared to make any extensive study of the questions opened by these results we have been forced to conclude for the present that the magnetic test alone gives only a qualitative indication of the presence of iron but no quantitative measure of the amount present.

The work of Isaac and Tammann (*Zett. Anorg. Chem.*, 1907, iv, 63) indicates the cause of the small magnetic effect produced by a considerable percentage of iron when dissolved in platinum. They have found that the magnetic transformation point, which is about 770° in pure iron, is rapidly lowered by the addition of platinum, until at 50 weight per cent platinum it is near 100°. Near pure

platinum it would seem to be below room temperature. It is possible, though not proven by their results, that the magnetisation of the alloys between 30 and 0 per cent of iron is due to an "α'-form" of solid solution crystals, with an inversion curve which falls rapidly with increasing iron content, just as the inversion curve of the α form of pure iron and of the iron rich alloys falls rapidly with increasing content of platinum.

**Cause of Reducing Action of Platinum.**—We have shown that platinum acts on both hematite and magnetite at 1200° under low pressures of oxygen, absorbing iron and giving off oxygen. It also reacts with magnetite in the same way at 1600° and at the usual atmospheric pressure of oxygen. (Hematite is not stable in air at 1600° but goes over into magnetite). On the other hand, it is well known to analysts that platinum crucibles in which  $\text{Fe}_2\text{O}_3$  is ignited in air for weighing in

analytical procedures take up no such amounts of iron as we have described in previous paragraphs. The reason for these differences of behaviour is readily found in the phase rule and the relations of iron and platinum in their alloys.

The system contains three components—platinum, iron, and oxygen. Iron and platinum form a continuous series of solid solutions. The oxidation of the iron causes it to separate from the platinum as an oxide. If we now have present the three phases—iron-platinum alloy, solid oxide, and gaseous oxygen—and assume a certain concentration of iron in the platinum (say 0.01 per cent) and a certain temperature (say 1200°), then there must be a definite oxygen pressure in equilibrium with this system. If the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidised, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced.

It is evident from the fact that melted magnetite is reduced by platinum in air that at 1600° the oxygen pressure of the air (about 152 mm.) is less than the oxygen pressure in equilibrium with dilute solutions of iron in platinum. Similarly, at 1200°, 18 mm. oxygen is less than the equilibrium oxygen pressure, and at this temperature and pressure iron is absorbed by platinum from all oxides between  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . The 152 mm. oxygen, however, is greater than the oxygen pressure of any but the most extremely dilute solution of iron in platinum at 1200°, and at this temperature, which is seldom exceeded in igniting iron oxide precipitates for analysis, there is no appreciable reduction of  $\text{Fe}_2\text{O}_3$  by platinum in the open air.

These considerations explain the very common occurrence of small amounts of iron in platinum, since platinum will exercise its reducing action on any material containing iron oxides with which it comes in contact, provided the temperature is sufficiently high. At low temperatures, on the other hand, and with abundant access of atmospheric oxygen, no appreciable reduction is to be expected.

## THE MANUFACTURE OF ACID PHOSPHATE.\*

By WM. H. WAGGAMAN, Scientist in Fertiliser Investigations.

(NOTE.—Describes the manufacture of acid phosphate from phosphate rock, detailing the chemical and mechanical changes involved. Of interest to fertiliser manufacturers generally).

### INTRODUCTION.

THE acid phosphate industry in the United States has grown to enormous proportions. In spite of the fact that numerous other forms of phosphatic fertiliser have been proposed or patented from time to time, and the application of raw ground-rock phosphates directly to the field has been recommended by some agronomists and agricultural chemists, the annual production of superphosphate continues to increase. There is little doubt, therefore, that this material will continue to be the basis of most of our commercial fertilisers.

While the general procedure followed in making acid phosphate is a familiar one, many of those engaged in the production of this material have but little knowledge of the chemistry involved and are unfamiliar with numerous details of its manufacture, which are of great economic importance (J. S. Brogdon, "Manufacture of Acid Phosphate," *Am. Fertiliser*, 1913, [5], xxxix., 25). Competition has become so keen in the fertiliser industry during the last few years that in order to make a reasonable profit the manufacturer can no longer afford to carry on his

business in the loose way formerly so prevalent, but must practise the most modern scientific methods and exercise the closest supervision over every detail of his factory processes. It is believed that the preparation of this Bulletin is justified by the information it will furnish the fertiliser manufacturer; but it is intended primarily to give the progressive farmer a clearer knowledge of that compound which is the basis of fertilisers, in order that he may more intelligently buy and handle his fertiliser and determine for himself its true value. Such knowledge, it is believed, should tend greatly to clarify prevailing ideas concerning the value of factory and of home-mixed fertilisers, and to throw light on the attendant question of inordinate profits alleged to be made by manufacturers. This paper describes the whole process, including the preparation of the raw materials used, the methods of manufacture with the chemical reactions involved, the equipment of the modern factory, the disposal of obnoxious gases, the methods of drying, storing, and disintegrating the superphosphate, and the cost and disposal of the finished product.

### RAW MATERIALS.

The raw materials used in the manufacture of acid phosphate are bone, guano, apatite, phosphate rock, and sulphuric acid.

Before the discovery of the vast deposits of phosphorites or natural phosphate rock in this country bone was one of the farmer's chief sources of phosphoric acid. The bones were either steamed, charred, or burned, and applied directly to the field, or after grinding were made into acid phosphate by treating with an approximately equal weight of sulphuric acid.

Ground bone, however, has considerable agricultural value without being acidulated, and besides, the cost of the phosphoric acid contained therein is so much greater than that contained in phosphate rock that it is obviously not economical to use the former material in the manufacture of acid phosphate. The amount of this substance now derived from bone is therefore relatively small.

Guano is another substance which has been extensively used in the manufacture of acid phosphate. This material consists essentially of the excrements of birds and sometimes of bats, and at one time was found in large quantities. There are two types of guano deposits:—1. The unleached deposits which are usually found in caves or other sheltered places where the droppings have been protected from the leaching effect of percolating water. Such a deposit not only contains phosphoric acid in a readily available form, but also carries considerable quantities of nitrogen, the fertiliser constituent commanding the highest price. 2. That which has been leached of its more soluble constituents by exposure to the weather. It contains practically no nitrogen and its phosphoric acid content, though usually high, is relatively insoluble. Deposits of guano have been eagerly sought, and accessible and valuable ones are now rather scarce. Only those containing high percentages of nitrogen, or situated in regions having excellent transportation facilities, are able to compete with other and cheaper sources of phosphate.

At one time apatite was largely used in the manufacture of acid phosphate. This mineral is very widely distributed, and occurs in rocks of various kinds and ages. It is most common, however, in rocks of the metamorphic crystalline variety, such as limestone, gneiss, mica, schist, beds of iron ore, &c. There are two main varieties of apatite, namely, chlor-apatite,  $\text{CaClCa}_4\text{P}_3\text{O}_{12}$ , and fluor-apatite,  $\text{CaFCa}_4\text{P}_3\text{O}_{12}$ . The latter variety is by far the most common, but there are intermediate compounds containing both chlorine and fluorine. Pure fluor-apatite contains 42.3 per cent phosphoric acid,  $\text{P}_2\text{O}_5$ , but it is seldom found in a pure condition. The occurrence of apatite associated with magnetite in northern New York has long been known (W. F. Blake, *Trans. Am. Inst. Min. Eng.*, 1892-93, xxi., 157), but attempts to separate the apatite commercially have proved unsuccessful.

\* Bulletin 144, U.S. Department of Agriculture, Bureau of Soils.

TABLE I. — Composition of Phosphatic Materials used in the Manufacture of Acid Phosphate.

Phosphatic material.	Location.	Nitrogen, N.	Silica or in- soluble, SiO <sub>2</sub> .	Oxide of iron and aluminium, Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> .	Calcium fluoride, CaF <sub>2</sub> .	Carbonate of lime, CaCO <sub>3</sub> .	Phosphoric acid, P <sub>2</sub> O <sub>5</sub> .	Tricalcium phosphate(s) Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Bone-ash . . . . .	—	4.06	3.01	—	—	5.28	35.38	76.65
Fat-extracted bone ..	—	4.14	3.60	—	—	5.24	21.68	46.50
Bone or animal charcoal	—	1.12	2.00	0.37	1.00	8.00	31.99	73.10
Apatite, high grade ..	Canada .. . . .	—	3.67	0.70	3.10	4.13	38.60	88.20
Apatite, lower grade ..	Canada .. . . .	—	8.92	1.03	3.04	8.05	34.42	78.65
Apatite, high grade ..	Norway .. . . .	—	3.62	1.37	2.62	0.29	39.44	86.10
Bat guano .. . . .	Porto Rico .. . .	8.35	—	1.59	—	—	7.57	16.52
Guano in crusts .. .	West Indies .. . .	0.45	—	5.88	—	—	24.36	53.18
Phospho-guano .. . .	Mexico .. . . .	0.40	—	1.14	—	—	39.70	86.66
Phosphorite, high grade	Somme, France .. .	—	0.79	1.39	—	9.17	35.59	77.69
Phosphorite, lower grade	Somme, France .. .	—	8.55	4.07	—	6.95	29.10	63.53
Phosphorite, lower grade	Liège, Belgium .. .	—	16.14	2.39	5.00	7.07	27.20	62.15
Coprolites .. . . .	Cambridge, England	—	9.00	—	—	2.30	34.00	77.70
Coprolites .. . . .	Suffolk, England ..	—	Not deter.	9.00	6.00	10.00	23.63	54.00
Phosphate nodules ..	Russia .. . . .	—	Not deter.	5.00	6.98	12.23	32.82	75.00
Phosphate nodules ..	South Carolina .. .	—	4.12	1.4	2.8	11.25	25.28	57.64
Hard rock phosphate ..	Florida .. . . .	—	4.13	3.00	4.40	3.63	36.39	83.14
Land pebble phosphate.	Florida .. . . .	—	5.10	1.4	0.3	2.5	30.34	69.78
Brown rock phosphate..	Tennessee .. . . .	—	2.5-10	3-8	0.5	0.10	30.38	69.87
Blue rock phosphate ..	Tennessee .. . . .	—	2.5-70	2.5-7	0.3	0.2	27.32	62.73
White rock phosphate..	Tennessee .. . . .	—	2-7.5	1.5-3.5	—	—	32.38	73.87
Black rock phosphate ..	Arkansas .. . . .	—	15-40	2.5-9.5	—	—	23.28	53.64
Brown rock phosphate..	Kentucky .. . . .	—	2-5	2.5-5	—	—	30.35	69.80
Oolitic black phosphate.	Utah, Idaho, &c. ..	—	1.8-10	0.07-1.6	0.8-1.35	3.8-13.6	27-36.5	62-83
White phosphate .. .	Ocean Islands .. .	—	Not deter.	0.42	1.0	4.91	38.73	84.65

(a) Known to the trade as bone phosphate of lime, b. p. 1.

In Norway and Canada, however, there are large deposits of apatite which were at one time extensively worked, but the discovery of cheaper and more accessible sources of phosphoric acid (particularly in the United States) has caused a serious curtailment in the mining of this mineral.

The main objections to apatite as a source of phosphoric acid are, first, the expense of mining and picking the rock, and, second, the large percentage of fluorine, which yields obnoxious gases when the rock is treated with sulphuric acid. The superphosphate now manufactured from apatite is but a small percentage of the total material marketed.

The vast bulk of acid phosphate produced both in this country and abroad is made from the amorphous phosphates of lime, of which there are enormous deposits in the States of Florida, Tennessee, Utah, Idaho, Wyoming, and Montana, and in northern Africa, and smaller deposits in the States of South Carolina, Arkansas, and Kentucky in this country, and in France, Germany, England, and Belgium.

Ocean and Pleasant Islands of the Gilbert group, as well as some of the Society Islands in the southern Pacific, and Christmas Island in the Indian Ocean, contain large quantities of very high grade phosphate rock; in fact, these phosphates are as rich as any amorphous phosphates known. It is only in recent years, however, that the deposits have been developed to any extent, and owing to the lack of harbours the rock must be loaded at sea, which makes their exploitation somewhat difficult.

The character of the American deposits, the methods of mining and preparing the rock for the market, the cost of production, annual output, and other details of this industry have been described in Bulletins of this department, and so need not be repeated here (*Bull.* 41, 69, 76, and 81, Bureau of Soils, U.S. Dept. Agr.; *Bull.* 14, U.S. Dept. Agr., 1913).

In Table I. is given a list of the more important phosphatic substances (with their approximate composition) used in the manufacture of acid phosphate.

The sulphuric acid used in the manufacture of acid phosphate is the ordinary "chamber acid." It ranges in specific gravity from 1.5 to 1.6 at 60° F., and contains

from 60 to 70 per cent of sulphuric acid. The fertiliser trade, however, is accustomed to expressing the strength of "chamber acid" in Baumé degrees (°B). The manufacturer should have conversion tables at hand showing the specific gravity and percentage of acid corresponding to each degree registered by the Baumé hydrometer. Part of such a table approved and adopted by the Manufacturing Chemists Association of the United States is given in Table II.

#### THEORETICAL BASIS FOR THE MANUFACTURE OF ACID PHOSPHATES.

The process of making acid phosphate was devised in order to change the phosphoric acid contained in the substances just enumerated into a more soluble or "available" condition.

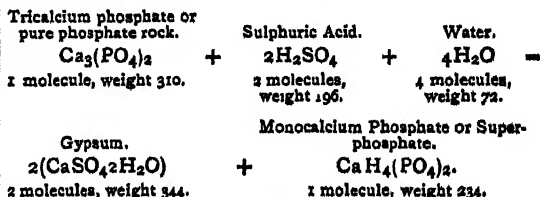
The phosphates of lime, as found in nature are highly basic compounds or solid solutions offering considerable resistance to the solvent influence of percolating meteoric or soil waters. The less basic phosphates (those containing less lime, iron, alumina, or magnesia) are more soluble in water (*Bull.* 41, Bureau of Soils, U.S. Dept. Agr., 1907). Therefore, in order to bring about the desired change, an acid stronger than phosphoric acid is added in sufficient quantity to combine with a portion of the lime, producing a phosphate less basic and, consequently, more soluble. The reagent which has been found best suited for this purpose is sulphuric acid, not only because of its cheapness but because calcium sulphate, one of the products of the reaction, takes up the excess of water present in the acid phosphate to form gypsum. The final product, therefore, if properly made, is dry and can be readily mixed with other ingredients to make a complete fertiliser.

The main purpose sought to be accomplished in the factory treatment of phosphate rock is to prepare a product in which the phosphoric acid will be water soluble, so far as this can be accomplished, with due regard to the physical properties of the product essential to its ready mixing and handling. While it is a matter of no great difficulty to determine by a chemical analysis just what constituents are in a given phosphate rock and in what

TABLE II.—Specific Gravities and their Equivalents in Baumé Degrees of Sulphuric Acid of various Strengths.

°B.	Sp. gr.	Per cent $H_2SO_4$
0	1.0000	0.00
1	1.0069	1.02
2	1.0140	2.08
3	1.0211	3.13
4	1.0284	4.21
5	1.0357	5.28
6	1.0432	6.37
7	1.0507	7.45
8	1.0584	8.55
9	1.0662	9.66
10	1.0741	10.77
11	1.0821	11.89
12	1.0902	13.01
13	1.0985	14.13
14	1.1069	15.25
15	1.1154	16.38
16	1.1240	17.53
17	1.1328	18.71
18	1.1417	19.89
19	1.1508	21.07
20	1.1600	22.25
21	1.1694	23.43
22	1.1789	24.61
23	1.1885	25.81
24	1.1983	27.03
25	1.2083	28.28
26	1.2185	29.53
27	1.2288	30.79
28	1.2393	32.05
29	1.2500	33.33
30	1.2609	34.63
31	1.2719	35.93
32	1.2832	37.26
33	1.2946	38.58
34	1.3063	39.92
35	1.3182	41.27
36	1.3303	42.63
37	1.3426	43.99
38	1.3551	45.35
39	1.3679	46.72
40	1.3810	48.10
41	1.3942	49.47
42	1.4078	50.87
43	1.4216	52.26
44	1.4356	53.66
45	1.4500	55.07
46	1.4646	56.48
47	1.4796	57.90
48	1.4943	59.32
49	1.5104	60.75
50	1.5263	62.18
51	1.5426	63.66
52	1.5591	65.13
53	1.5761	66.63
54	1.5934	68.13
55	1.6111	69.65
56	1.6292	71.17
57	1.6477	72.75
58	1.6667	74.36
59	1.6860	75.99
60	1.7059	77.67
61	1.7262	79.43
62	1.7470	81.30
63	1.7683	83.34
64	1.7901	85.66
64½	1.7957	86.33
64½	1.8012	87.04
64½	1.8068	87.81
65	1.8125	88.65
65½	1.8182	89.55
65½	1.8239	90.60
65½	1.8297	91.80
66	1.8354	93.19

proportions, it is not known just how these constituents are chemically united. It is generally assumed that the phosphoric acid is combined with the lime in a hypothetical compound—tricalcium phosphate (known to the trade as bone phosphate of lime, b. p. 1.), represented by the formula  $Ca_3(PO_4)_2$ , and that this compound, when treated with sulphuric acid,  $H_2SO_4$ , and water,  $H_2O$ , in the right proportions, is converted into a mixture of gypsum,  $CaSO_4 \cdot 2H_2O$ , and monocalcium phosphate,  $Ca(H_2PO_4)_2$ . Both gypsum and monocalcium phosphate are perfectly definite, well-known compounds. The former is but slightly soluble, the latter readily soluble in water. As a matter of fact, in the reaction cited above, it is probable that dicalcium phosphate,  $Ca(HPO_4)_2$ , is formed as well. Both these calcium phosphates are decomposed by water, so that a solution of monocalcium phosphate, if diluted, will precipitate dicalcium phosphate, and if the dilution be carried further, a phosphate even more basic than the tricalcium phosphate is formed (*Vide, Bull. 41, Bureau of Soils, U.S. Dept. Agr., 1907, p. 22*). Obviously, the more basic the calcium phosphate, the less soluble it is in water. It is equally obvious that when incorporated in the soils, the soil water, while dissolving and distributing the phosphate, is at the same time decomposing it into less soluble forms. Assuming now, as we may do for convenience, that the reaction takes place in the mixing as outlined above, it may be represented thus:—



The above equation means that in order to change completely 310 parts of tricalcium phosphate or pure phosphate rock into acid phosphate, 196 parts of *pure* sulphuric acid are required, or 1 ton of phosphate rock requires 0.63 ton of sulphuric acid. Factory practice and long experience in the manufacture of acid phosphate have shown, however, that much better results are obtained by employing sulphuric acid containing from 30.35 to 37.82 per cent of water ("chamber acid"). A part of the water contained in this acid is evaporated by the heat of the chemical reactions taking place, and a part is taken up by the calcium sulphate formed to produce gypsum, as shown in the above equation.

#### IMPURITIES IN PHOSPHATE ROCK.

Besides calcium phosphate the phosphates of commerce always contain varying quantities of impurities, such as organic matter, silica or silicates, calcium fluoride, oxides or phosphates of iron and aluminium, and carbonates of lime or magnesia. All of these impurities take up or are acted upon directly or indirectly by sulphuric acid, the bases being converted into sulphates, and the fluorides, carbonates, and organic matter being decomposed with the evolution of gases. It is very important that the manufacturer should be acquainted with the effect that these impurities and the compounds produced therefrom will have upon his acid phosphate, and he should be able to calculate from the analysis of his raw material what quantity and strength of sulphuric acid is required to satisfy these impurities. The action of the sulphuric acid upon the various foreign substances found in natural phosphates of lime and the effect of these impurities on the finished product are discussed below in some detail.

#### Organic Matter.

Practically all phosphates, with the exception of apatite are of animal origin and therefore contain a certain amount of organic matter. When present in any quantity

organic matter usually imparts a dark colour to the phosphate. The presence of very small quantities can be detected by the putrid odour emitted on crushing or grinding the rock. The phosphates of our Western States, as well as some of the Tennessee rock, contain considerable quantities of organic matter, while most of the Florida phosphates are very low in this material.

The methods now employed in drying phosphate, either by calcining it on ricks of wood or putting it through a rotary drier, burns out or destroys a part of the organic matter; the remainder is carbonised by sulphuric acid with the evolution of volatile or gaseous products. The sulphuric acid is at the same time reduced to sulphur dioxide,  $\text{SO}_2$ , or to hydrogen sulphide  $\text{H}_2\text{S}$ , if the reduction has proceeded further. The production of these gases not only entails a loss of sulphuric acid, but they are both disagreeable and deleterious to health.

In making acid phosphate the organic matter found in the rock is not considered, since the amount present is usually small. Owing to the various forms in which organic matter may occur, it is almost impossible to judge except by actual experiment how much sulphuric acid is required for its decomposition.

#### Silica and Silicates.

Sulphuric acid has no direct action upon silica,  $\text{SiO}_2$ , but when fluorides are present an indirect action occurs, which is described below. Silicates are directly acted upon by sulphuric acid, but so slowly that they need hardly be taken into account. The presence of silica or silicate minerals in phosphate rock is not considered objectionable except in so far as they act as diluents. Phosphates containing high percentages of silica necessarily have a lower percentage of phosphoric acid than the less siliceous or purer phosphates.

#### Calcium Fluoride.

Fluorides are present in almost all phosphate rock. Some samples contain as high as 8 per cent of calcium fluoride,  $\text{CaF}_2$ . The amorphous phosphates as a rule contain smaller quantities of this compound than apatite.

Calcium fluoride reacts with sulphuric acid, giving gaseous hydrofluoric acid,  $\text{HF}$ , and calcium sulphate, thus:—

Calcium fluoride. Sulphuric acid. Hydrofluoric acid. Calcium sulphate.  
 $\text{CaF}_2 + \text{H}_2\text{SO}_4 = 2\text{HF} + \text{CaSO}_4$

But hydrofluoric acid,  $\text{HF}$ , acts upon the silica or silicates present in the mass, producing gaseous silicon tetrafluoride,  $\text{SiF}_4$ , and water or steam, thus:—

Hydrofluoric acid. Silica. Silicon tetrafluoride. Water.  
 $4\text{HF} + \text{SiO}_2 = \text{SiF}_4 + 2\text{H}_2\text{O}$

Silicon tetrafluoride in turn is decomposed by water with the formation of hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ , and precipitation of pure silica,  $\text{SiO}_2$ , thus:—

Silicon tetrafluoride. Water or Steam. Hydrofluosilicic acid. Silica.  
 $3\text{SiF}_4 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SiF}_6 + \text{SiO}_2$

Before this last reaction takes place, however, much of the silicon tetrafluoride escapes from the mass and can be detected by its penetrating odour and smarting effect on the eyes and nose.

Very high grade acid phosphate can be made from rock containing large amounts of fluorine, because, as pointed out above, many of the products formed during the process escape as gases or vapours, leaving the mass correspondingly richer in phosphoric acid. These gases also, in forcing their way out of the acid phosphate, tend to render it porous and more readily dried. The product, therefore, can be easily broken up and mixed with other ingredients to make a complete fertiliser.

The main objections to using phosphates high in fluorides are, first, the increased quantity of sulphuric acid necessary to decompose these compounds, and, second, the noxious and even poisonous nature of the gases evolved during their decomposition.

(To be continued).

#### WELSH NOTES.

(By Our Special Correspondent).

SWANSEA dock trade maintains an excellent increase notwithstanding the bad times, and we find an increase of 31,000 tons in the tonnage dealt with last week as compared with the corresponding week in last year. The import trade was very active, so active in fact as to bring the net tonnage to an increase of 10,000 tons over the preceding week, in which the import trade had been comparatively quiet. Among the exports patent fuel did not maintain the activity of the past few weeks, but was nevertheless considered eminently satisfactory. Chief among the imports were:—446 tons scrap steel, 1530 tons of zinc ore from France, 15 tons tin ore, 2080 tons iron pyrites, and 3710 tons copper ore from Spain, copper matte 330 tons, and nickel matte 30 tons. Shipments of tinplates amounted to 86,834 boxes, 74,000 boxes being received from works. Stocks in the dock warehouses and vans amounted to 295,358 boxes, compared with 308,185 boxes the previous week and 228,947 boxes in the corresponding week of last year. Of patent fuel 14,155 tons were exported.

All the varied trades of the Swansea and adjoining valleys with the exception of the tinplate and sulphuric acid works displayed considerable activity throughout the week. Great pressure was noticed at Baldwin's blast-furnaces, and it is said that the output well exceeded expectations. So busy were the steelworks that arrangements have been made with the men to put in twelve hours per day to cope with the production of material required by the Government. The copper industry had a good week, and the tonnage of copper plates was exceptionally heavy. The spelter trade experienced even greater pressure than that of the past few weeks. Government work was in evidence on every hand, and very little work of any other kind was seen, local orders being forced to take second place. The quietness experienced in the tinplate trade saw the temporary closing down of the Forest Works over the week-end, affecting some 200 or 250 men. There was a good supply of lead-piping and safety fuse, and these passed off with a quiet demand. Full pressure was experienced at the Mond Nickel Works and the Mannesman Tube Works, every department being exceptionally busy. The Metal Extraction Works were engaged for a full week, whilst iron and brass foundries were satisfactory.

The Dowlais Iron and Steel Works have experienced a very busy week, all furnaces and mills being engaged to full capacity. The Goat Mill turned out a heavy amount of tonnage of heavy pattern steel rails, billets, steel sleepers, and square bars. The Big Mill was engaged in fish plates, sole plates, tram rails for underground use, and sidings.

Port Talbot Docks had a fairly good week, an aggregate of 54,493 tons being dealt with. Among the exports, which consisted mainly of coal, were 2460 tons of patent fuel and 1223 tons of copper ore ranked among the imports.

How the war may result in British producers capturing some of the German spelter trade was mentioned at the thirty-second general meeting of shareholders in the English Crown Spelter Co., Ltd., held at Port Tennant, Swansea, on Friday. Mr. Reginald Francis, Chairman, said that, as perhaps one of the largest producers of spelter in this country, they were doing their fair share towards helping the nation to win the war, and wished they could do more. They wanted, after the war, to take the position that Germany had held in buying Australian ores, smelting them in Germany with English coal of high quality, and selling the resulting metal to us in England at a profit.

In reply to a question as to the position of the company's mines in Italy now that war had been declared, the Chairman said he did not think any warlike preparations would affect the mines at all, but it was possible that labour



would be affected as also might transport. They had other sources of supply outside their Italian mines which would keep them satisfactorily supplied for some time to come, besides which they had stocks to carry them fairly well towards the end of the present year. Continuing, the Chairman said they would have noticed an advance in the price of spelter, and this could not fail to benefit the company. They had been in touch with some important financial groups in London with regard to the large productions of zinc concentrates in Australia which in the past had been treated mostly in Germany, but existing contracts were under the consideration of the British and Australian Governments. Their directors had not lost sight of the probable alterations in the world's markets, and had already in hand preparations for the installation of two additional smelting furnaces.

## NOTICES OF BOOKS.

*List of Reagents for Analytical Purposes.* London: The Institute of Chemistry. 1915.

THIS list of purified reagents which can be obtained from British merchants, although it does not claim to be complete, gives a very fair idea of the extent to which the requirements of chemists can be satisfied by fine chemicals made in Great Britain. The standards of purity to which each article attains are explained in detail, the tests described being mainly those adopted by a Committee appointed by the Eighth International Congress of Applied Chemistry. It is earnestly to be hoped that merchants will do their utmost to encourage trade in British made chemicals, even at the cost of some little inconvenience at first, so that we may ultimately become quite independent of foreign firms.

*The Electric Furnace in Metallurgical Work.* By DORSEY A. LYON, ROBERT M. KEENEY, and JOSEPH F. CULLEN. Washington: Government Printing Office. 1914.

THIS bulletin is a very complete compilation of data connected with the construction and uses of the electric furnace, electrothermic methods being chiefly described; i.e., those in which the current is used as a source of heat. Only processes involving the reduction of an ore to a metal or the preparation of a valuable compound of a metal are included. In Part I. the essential features of the electric furnace are explained, and some account is given of the cost of electric power and the factors influencing it. The application of the electric furnace in metallurgy is then treated, much attention being paid to the ferro alloys, while iron itself is discussed in outline only, having been the subject of a previous bulletin. Some details of several European plants are given, and also full information regarding the uses of each ferro alloy.

*Jac. Berzelius Bref.* ("Letters of Jac. Berzelius"). Vol. IV. Upsala: Almqvist and Wiksells Boktryckeri-A.-B. 1915.

THIS volume of Berzelius's letters contains all those which passed between him and Dulong during the period 1819—1837. Most of them are now published for the first time. They give an interesting view of Berzelius's keenness and energy in scientific work, and of Dulong's devotion to research and the difficulties under which he laboured owing to his ill health and his uncongenial teaching work. Berzelius's letters contain accounts of his investigations of sulphocyanides, silicon, fluoric acid, &c., and discussions of many of the scientific theories put forward in his day; the letters on both sides were written in French, and are reproduced in full with the addition of some notes.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clx. No. 19, May 10, 1915.

**Chemical Study of Coloured Glasses of the Middle Ages.**—G. Chesneau.—The author has studied the chemical constituents of coloured glasses from Rheims Cathedral. He finds that violet glass, besides manganese in the form of  $Mn_2O_3$ , always contains iron oxide and traces of copper and cobalt, which are the elements generally associated in impure pyrolusites. Blue glass contains the elements found together in native arsenio-sulphide of cobalt, and has thus been coloured with zaffre obtained from this mineral. Nickel produces a dark brown coloration, and the absence of nickel in the specimens analysed shows that in the thirteenth century it was known how to avoid the presence of nickel in zaffre. The colour of green glass was produced by mixing oxides of copper and iron, a small amount of cobalt and a good deal of manganese being also present. Red glass was obtained by a very thin layer of enamel, which was coloured with cuprous oxide.

**Dioxytriazines. Synthesis of Substituted Semi-carbazides.**—J. Bougault.—When the mono-ethers of benzylodioxytriazine are boiled with dilute soda substituted semicarbazones of phenol pyruvic acid are obtained. The corresponding alkylsemicarbazides may be prepared from them by the action of cold concentrated hydrochloric acid. These alkylsemicarbazides are crystalline substances which appear to be fairly stable. They are very soluble in water, alcohol, and chloroform. They give crystallised hydrochlorides soluble in water and alcohol. Towards aldehydes and ketones they behave like semicarbazide itself.

## MISCELLANEOUS.

**New Method of Determining Sodium and Potassium in a Mixture of their Salts.**—Kichiro Okada.—When a given quantity of a mixture of sodium and potassium salts is mixed with a given quantity of sodium hydrogen tartrate in solution, and the temperature and total volume of the solution are kept constant, the concentration of the tartrates remaining in the solution is a function of the percentage of potassium in the sample. If this function be given in the form of a curve, a mixture of sodium and potassium salts may be analysed by determining the concentration of the tartrates remaining in the solution. The author has determined the standard curve by dissolving 1 gm. of the mixed chlorides of known composition and 2.4 grms. of sodium hydrogen tartrate in water, diluting to 50 cc. at 25° C., and keeping at that temperature for five hours. Then 20 cc. of the clear solution were evaporated to dryness and brought to a red heat. The alkalis were extracted with a known volume of standard  $HCl$  and the excess of acid back-titrated. The quantity of  $HCl$  was plotted along the ordinate axis and the percentage by weight of sodium chloride along the abscissa axis. This method of analysis was found to be tolerably reliable for ordinary purposes.

**Double Salt of Sodium and Potassium Sulphates.**—Kichiro Okada.—Using the analytical method just described, the author has studied the composition of the double salt of sodium and potassium sulphates. He has found that its formula is  $K_3Na(SO_4)_2$ . It dissolves in sodium sulphate as a solid solution, but not in potassium sulphate.—(*Memoirs of the College of Science, Kyoto Imperial University*, i., No. 2).

# THE CHEMICAL NEWS.

VOL. CXI., No. 2900

## MASS AND WEIGHT.

By F. H. LORING.

IN speaking of the *ratio of mass to weight becoming unity* (CHEMICAL NEWS, cxi., p. 157: end of art.), a misconception of the intended meaning is possible, since "the ratio of weight to mass is often called the intensity of gravity, and denoted by  $g$ ."

It may not be out of place in a discussion of mass and weight to give first a statement of mass, which is based upon an early definition in Rodwell's "Dictionary of Science" (1873), but with some alterations in the wording and a few enlargements.

Mass is a term for the quantity of matter in a body. In order to measure mass, it is assumed that the attraction of the earth on all particles of matter is the same whatever may be their physical state or arrangement, and this attraction is also the same irrespective of their chemical nature. This assumption is fully justified by the fact that bodies of all shapes and of all kinds and sizes fall with equal velocity in the exhausted receiver of an air-pump. This comparative equality of velocity when different bodies are dropped together holds true at all latitudes, though both the centrifugal force due to the rotation of the earth and the gravitational attraction vary according to the latitude of the place. If a one-pound mass at a given place fell slower than a two pound mass at the same place, we should, upon dividing the latter into two one-pound parts, have to account for a miraculous disappearance of force; hence the equality in velocity arises from a given force acting with a given amount of matter. Therefore we are able to measure the mass of a body by its weight, using for this purpose a counterpoise balance, and we can only define the mass as a quantity proportional to the weight, in the sense that if at a given place on the earth's surface one body is twice as heavy as another the mass of the first is twice that of the second. Suppose, however, that the body be weighed by a spring-balance at a certain place removed from the Equator, and weighed again by the same instrument at another place on or near to the Equator, it will be found that the body is lighter at the latter place. It is found, too, that the acceleration due to the force urging the body towards the earth is also less at the second place than at the first, in the same proportion. This illustrates the fact that when the mass remains the same the weight varies as the acceleration of gravity.\* Hence the weight varies as the product of the mass and this acceleration, and consequently, when suitable units are chosen, the mass of a body is equal to its weight divided by the acceleration due to gravity. Acceleration is the rate of increase (or change) of velocity per unit of time (see below). We may observe that if the acceleration due to gravity were taken as unity, then the mass would numerically equal the weight, and the ratio would be unity.

Going over familiar ground, we of course know that the *kilogramme* is defined as the mass of a piece of platinum deposited for safe keeping in the Archives of Paris, and that the standard unit in the *Centigrade-Gramme-Second* system is a *thousandth* part of this mass = *one gramme*.

At Paris the acceleration of gravity ( $g$ ), as it is termed,

\* The term *gravity* as thus used is not a pure term, but involves in practice the diluting effect of centrifugal force. This does not matter, since all forces can be added to or subtracted from each other as if they were of the same kind. It may be more satisfactory to say they are *superposed*, in which case the cancelling out or augmenting, as circumstance demands, leads to the same numerical or practical result. Forces acting in different directions give rise to a resultant force, so that we may say that forces are often resultant effects.

is such that the gramme-mass (or any other mass) will fall there under the influence of the earth's attraction, when dropped from a height, with a velocity of  $981.0^*$  centimetres per second at the end of the first second, at the end of the second second  $2 \times 981$ , at the end of the third second  $3 \times 981$ , and so on.

Suppose that we cinematograph a falling watch against a stationary measuring rule or scale 256 ft. long. We shall find that at the 16-ft. mark on the rule the watch registers one second in advance of its time when liberated. The watch has taken one second to cover 16 ft. During consecutive seconds it will have traversed 16, 48, 80, and 112 ft. respectively (neglecting fractional values), the total distance traversed being the sum of these. If the watch had attached to it a speed-indicating mechanism, actuated, say, by a pinion engaging with a rack alongside the rule, then we should find that just at the end of each successive second it had indicated a velocity of 32, 64, 96, and 128 ft. per second respectively.

This will be understood from the following analysis:—

The velocity at the end of 16 ft. must be greater than 16 ft. per second, taken as an instantaneous velocity at this point; it is 32, as we shall see in the next paragraph.

The acceleration being *uniform*, we can say that 16 ft. per second represents a mean value; hence the maximum velocity, occurring at the end of the first second, would be  $16 \times 2 = 32$  ft. per second.

Similarly, at the end of the second second the total distance traversed would be  $16 + 48 = 64$  ft. This also being a mean value for two seconds, the maximum velocity then becomes  $64 \div 2 = 128$  ft. per two seconds. Since we are only concerned with the velocity per second at the end of the second second, this would be  $128 \div 2 = 64$  ft. per second.

To continue: at the end of the third second the total distance covered from the start would be  $16 + 48 + 80 = 144$  ft. The maximum velocity =  $144 \div 2 = 288$  ft. per three seconds. The time taken being three seconds, the velocity per second at the end of the third second would be  $288 \div 3 = 96$  ft. per second . . . and so on.

Now, during each successive second the gain per second has been 32 ft., since

$$\left. \begin{array}{l} 32 - 0 = 32 \\ 64 - 32 = 32 \\ 96 - 64 = 32 \end{array} \right\} = g$$

so that we may say the *acceleration per second per second* is 32 ft., and that it is *uniform*. The exact figure is practically 32.2 ft. per second per second at London, or 981 cm. per second per second at Paris.†

This means that the force acting downwards on the gramme mass is 981.0 dynes, because force = mass  $\times$  acceleration, the *dynes* being the unit of force which causes unit acceleration in unit mass, or, from another point of view, a unit force of 1 dyne is that force which, acting on unit mass for unit time, causes it to move with unit velocity. It is of course understood that in this case the unit of distance or length is the centimetre, the unit of mass is the gramme, and the unit of time is the second.

Since force = acceleration  $\times$  mass, and as the mass remains constant—in this case unity— $981 \times 1 =$  force of gravity, as it is termed. The acceleration is also constant; therefore the force must have acted with the same pull at the outset—that is, before the mass started on its downward movement; hence the force is the weight of the stationary mass of 1 gm. expressed in dynes.

\* The exact value is 980.94, corrected for sea level. The actual value, not so corrected, is 980.96, the altitude of Paris being 72 metres.

† It is of possible interest to note that the distances 16, 48, 80, 112, &c., stand to each other as the numbers 1, 3, 5, 7, &c., while the velocities at the ends of the consecutive seconds stand to each other as the numbers 1, 2, 3, 4, &c., and the distances ( $D$ ) from the beginning (each time taken) are the squares of the numbers 4, 8, 12, 16, &c.  
 $D = \frac{1}{2}gt^2$ .  $t$  = time in seconds.

$t = \sqrt{D \div \frac{1}{2}g}$ . Final velocity in ft. per sec. =  $\sqrt{D \times 8}$ . 8 is the square root of  $2g$ .

Mechanical friction due to the speed-indicator, as well as to air friction, is of course taken as a negligible quantity in discussing main principles.

At the Equator it is interesting to observe that the gramme standard of platinum will be pulled downwards with a force of 978.1 dynes. At the Pole the value becomes 983.1.

We speak of *downward* pull, but in truth both bodies pull equally on each other, just as in chemical actions we say A has an affinity for B, meaning that B has the same affinity for A: they act conjointly on each other. Bodies are known to attract each other in proportion to their masses (as the product of their masses), and the attraction varies as the inverse square of their distances from each other. One can imagine two stationary bodies of equal size and density in space pulling on each other by gravitational attraction, so that if free to move they would gravitate with equal velocities towards each other. In this case, as in all cases of classical dynamics, the attraction is considered mutual. Should one body be much larger than the other they would still pull with equal force on each other, though the movement of the smaller body would be greater than that of the larger, assuming that they are free to move. Now, suppose such a system to be set in rotation, so that the smaller body tends to fly away from the larger one situated on the axis of rotation. Assuming the same relative positions as before, the gravitational attraction would still be exactly the same, but superposed on this is a centrifugal force which prevents the smaller body from falling towards the larger one with the same velocity as when no rotation takes place.

At any particular instant of time during the "fall" would the two forces be exactly equal? That is to say, would the smaller body pull the larger body towards it with exactly the same force as that with which the larger body pulls the smaller?

It would seem that in this case the pull would be mutual and exactly equal as before, therefore the force of gravity is not in a sense essentially different from centrifugal force. This leads therefore to the conclusion that inertia of matter and gravitational attraction are allied phenomena, and represent negations of the same order, so that one is just as mysterious as the other. In this field we cannot apparently solve one problem or explain one phenomenon without solving or explaining several. There is also the principle of two forces acting in a *superposed* sense, and this may be an important consideration from a certain point of view.

The force of gravity would be absolutely the same at the Equator as elsewhere on the surface of the earth if it were a true homogeneous sphere in space, not under rotation and removed from other large bodies of space that might exercise a disturbing influence. As we know that the earth is not a true sphere—being an oblate spheroid—and that it is under rotation, the centrifugal force becomes greater at the Equator than elsewhere, and for this latter reason mainly the force of gravity is apparently less there.

Altitude and latitude must obviously be taken into account. The value of  $g$  is closely calculable from the experimentally-derived formula—

$$g = 980.6056 - 2.5028 \cos 2\lambda - 0.000003h,$$

$\lambda$  denoting latitude and  $h$  the height of the station (in centimetres) above sea-level.

Another formula is—

$$g = 978.07 + 5.08 \sin^2 \lambda - 0.000003h,$$

978.07 being the value taken for  $g$  at the Equator at sea-level.

In some calculations the radius of the earth at the place considered is taken into special account.

Irregularities in land contour introduce small variations, and these are sometimes allowed for. The disturbing influence of the sun and moon are too small to be considered except in cases of very large masses, such as the ocean. The tides show the effect of these extraneous forces, as we may conveniently speak of them.

Although the attraction at the Equator is reduced in effect, we need not alter the gramme-mass to conduct accurate weighings, since it is obvious that an arm or

counterpoise balance will enable the same quantities of material to be accurately dispensed there as elsewhere. A spring-balance would do, if calibrated at the Equator with a duplicate standard mass from Paris, as we have already practically indicated. Spring-balances are not, of course, sensitive and reliable instruments for accurate work.

The centrifugal force due to the orbital motion of the earth round the sun is of practically negligible magnitude from our point of view, since it does not produce a very appreciable variation of  $g$ .

While it is usual to speak of mass as weight or *vice versa*, there is, as we have seen, a fundamental distinction, and consequently it may be of interest to restate the relations based upon the second law of motion in view of our original argument.

Let  $w$  = "pull to earth" in dynes at the place considered.

Let  $m$  = mass in grammes (Paris standard).

Let  $g$  = the velocity in centimetres per second at the end of one second imparted to the standard mass of 1 gm. (or, in fact, any mass) at the place considered = the acceleration in centimetres per second per second (see above).

Then—

$$w = m \times g \text{ and } w/m = g.$$

Taking figures, and assuming that  $m$  represents the mass, i.e., the unknown quantity to be found from the other two values, we have—

$$981 = m \times 981,$$

$m$  therefore = 1 = mass of gramme weight, which defines the mass as being a weight, as it were, which may be used to counterpoise a force of 981 dynes.

One kilogram. =  $10^3$  grms. =  $9.81 \times 10^3$  dynes in the C.G.S. system,  $g$  being taken as 981.

Returning now to our original statement of mass to weight being of unity ratio, we were considering a change or transformation in matter itself, so that originally it had not the property of gravitational attraction at all. Having, however, three dimensions, we could regard it as a sort of primary substance in a relative sense, keeping to our theory, and if such a substance could be placed on the pan of a balance (disregarding secondary disturbing effects), no weight could be measured by the Paris gramme standard, yet such a substance may have mass—perhaps electromagnetic mass—in a sort of inertia or momentum sense equal to, or perhaps greater than, the mass of the counterweight; hence we could say that if this primary substance could be transformed by a time influence, its weight would equal its mass, and the unity ratio would have a real significance, notwithstanding the relation  $w = m \times g$ , which is difficult to reconcile with electromagnetic mass, or with mass existing without weight (?). This might constitute electromagnetic mass, if we consider the  $\beta$ -particle (negative electron) as having electromagnetic mass and the  $\gamma$ -particle (X-ray) as a  $\beta$ -particle which has lost its electro-

\* We know that light is an electromagnetic wave phenomenon, and that it exerts pressure. On very minute particles of matter it may, under certain conditions, exert a pressure greater than gravitational attraction. While this pressure effect does not necessarily contribute to the argument that light is a corpuscular phenomenon (wave motions are known to give rise to a forward pressure) the light rays may be vortex rings of energy (atoms) which alternately thread through each other, expanding and contracting, thus giving rise to a periodic phenomenon that may be treated as an electromagnetic wave motion of an all-pervading aetheric medium, which in reality does not perhaps exist as such. It is as if we could take the long drawn-out lines of magnetism of a magnet or coil and weave them into a fabric comprising minute closed-up vortex coils; then as this fabric is manufactured at the light source and hurled out "broadside on," its coils undergo a sort of Brownian movement in threading through each other, expanding and contracting in the process. We certainly could not conceive ordinary matter going through such peregrinations, and in this sense the electromagnetic mass may be equally removed from ordinary mass as we experience it. From the study of radiation we might also conclude that light or radiation pulses react on matter, so that action is equal to reaction, otherwise we should have to question the validity of Newton's third law of motion.

magnetic mass entirely, and gained a corresponding amount of weight-mass. Are we not here dealing with a *material* end of the spectrum? This, of course, takes us beyond standard mechanics, or classical dynamics, as we should say.

Stated in another way, we may consider a gramme standard of platinum transformed back into a weightless substance, but having, say, electromagnetic mass; such a substance we cannot weigh, though we might somehow estimate its electric mass. Imagine this now placed upon the pan of a balance with a gramme standard on the other pan. No weight is registered, as it were. Now, suppose that this substance is transformed back (*in situ*) and that it then balances the gramme standard mass, we should then commonly say that it possessed a weight of 1 grm., and, being equivalent in every way to the counterpoise, we should also say that it had a mass of 1 grm. Therefore, by this argument, the ratio of its mass to its weight has become unity.

If we now consider our weight removed to a place in space (1) where there is no reacting gravitational field or (2) where the forces cancel out so as to exert no directive gravitational pull on matter, we should say in the ordinary way that the ratio of weight to mass had become infinity.

In this first case, what has become of the weight that was brought into existence by the transformation? Is it possibly there in some other form? Or, under such circumstances, have we to consider mass and weight in some sort of relativity sense? Or, again, does this argument prove the absurdity of the transformation idea, and signify that weight is a meaningless term by itself as distinguished from mass, which seems relatively a real entity independent of place? The second case is equally difficult of comprehension on the basis of a transformation.

The latter inferences seem the most rational in some respects. The term *weight* is not in the sense implied by the transformation a capacity term or vehicle like a quart cup that will hold a quart of liquid, but a sort of relative, or, rather, dependent capacity-like term, just as the carrying power of a floating vessel depends not upon its size only, but upon the density of the supporting medium (the analogy is imperfect), so that the transformation has evidently brought about a condition or state of matter whereby its capacity to acquire weight when brought into a gravitational field is proportionate to the masses involved.

No special physical meaning is here attached to the term *gravitational field*. It may be taken to represent three-dimensional space around bodies and across which they attract each other; the so-called intensity of field is commensurate with the masses, and therefore, strictly speaking, is not an attribute of space, though it is convenient to employ this term. We need not refer here to the variation due to distance, since this is implied in the geometry of space.

There is one other consideration that might be important when studying problems such as the evolution of matter, and that is that the fundamental units to be derived experimentally from Nature (as distinguished from our present artificial system) may ultimately involve us in the conception of unity values below which we cannot go, so that even acceleration of gravity in such a system might be 0 or 1 or 2, and so on. Unity ratios might somehow obtain as a first step in a process of accretion of matter, and in this fundamental sense, such units would be of the nature of natural quanta.

**Basic Salicylates.**—Echsner de Coninck and M. Gérard.—The substituted salicylic acids, like the acid itself, give basic salts of the type  $C_6H_4 < \begin{smallmatrix} CO_2 \\ O \end{smallmatrix} > Mn$ . All these salts are amorphous, insoluble or hardly soluble in water, insoluble in the principal neutral solvents, soluble in mineral acids. When dried and calcined they readily char; when moistened and heated they liberate phenol.—*Comptes Rendus*, cix., No. 19.

## BORNITE AS SILVER PRECIPITANT.\*

By CHASE PALMER,  
United States Geological Survey.

IN an introductory chapter of their studies in silver enrichment, Palmer and Bastin ("Metallic Minerals as Precipitants of Silver and Gold," *Economic Geology*, 1913, viii., 140) by quantitative experiments have shown that chalcocite ( $Cu_2S$ ) is decomposed completely by a dilute solution of silver sulphate. As a result of this reaction all the copper of the chalcocite enters the solution as cupric sulphate, while free silver and silver sulphide in equivalent amounts are deposited. Many years ago R. Schneider (*Pogg. Ann.*, 1874, clii., 471) recorded a similar observation on the conduct of cuprous sulphide ( $Cu_2S$ ) with dilute silver nitrate solution, but inasmuch as other observers have issued conflicting statements concerning the products of the reaction, it seemed advisable to study the reaction anew with silver sulphate solution. According to these recent experiments the proportions of the substances appearing in the reaction between chalcocite and silver sulphate solution may be expressed by the abbreviated equation  $Cu_2S + 2Ag_2SO_4 = 2CuSO_4 + 2Ag + Ag_2S$ .

Anthony (*Journ. Prakt. Chemie*, 1837, x., 353) had observed that by interaction with silver nitrate solution pure cupric sulphide ( $Cu_2S_m$ ) is changed completely to silver sulphide and soluble cupric nitrate without deposition of free silver, and this observation has been repeatedly confirmed by others. As a precipitant of silver ore, therefore, 1 grm. of pure covellite is capable of depositing 2.26 grms. of silver in the form of silver sulphide. On the other hand, 1 grm. of pure chalcocite is capable of precipitating 2.7 grms. of silver, one-half of which is combined with sulphur as silver sulphide and the other half is free silver.

Conspicuous among the more complex sulphides commonly associated with native silver is bornite. The mineral contains copper, sulphur, and iron, but its chemical composition has not been definitely settled. Analyses of bornite from different sources have led to several empirical formulæ for it, such as  $Cu_3FeS_3$ ,  $Cu_2FeS_4$ , and  $Cu_{12}Fe_2S_9$ .

The constitution of bornite has been a favourite subject of speculation. The views of Rammelsberg and Groth illustrate the vacillations and uncertainties likely to follow sole reliance on composition as indicative of constitution. In 1841 Rammelsberg assigned to bornite the constitutional formula  $3Cu_2S.Fe_2S_3$ , by which all the copper is represented as present in the cuprous state. Later he considered all the iron of bornite to be ferrous iron and the copper to be partly cuprous and partly cupric, and to express these supposed conditions he ascribed to bornite the constitutional formula  $Cu_2S.CuS.FeS$ . Groth has considered bornite to be strictly a cuprous substance, and has adopted the formula  $3Cu_2S.Fe_2S_3$  which Rammelsberg had abandoned.

It has been known for a long time that bornite immersed in a silver nitrate solution quickly develops on its surface a crop of silver crystals, but beyond the mere appearance of silver on bornite this striking phenomenon seems to have received no attention from mineralogists. Believing that a study of the capacity of bornite as a silver precipitant might throw light not only on the chemical composition of the mineral but also on the intramolecular relations of its constituents, the reaction of a specimen of bornite from Virgilina, Virginia, and dilute silver sulphate solution has been studied quantitatively. The specimen was massive, its freshly broken surfaces having a uniform colour. Metallographic examination of polished surfaces showed the presence of a few small grains of chalcocite and a few gashes of a dark grey mineral suggestive of chalcocite. The mineral was broken into small fragments,

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and from these were chosen only those pieces in which under the magnifier no chalcocopyrite could be detected. The granular pieces were washed with alcohol, and from these a second selection of bornite was made. In this way, it was believed, material representative of the true bornite in the specimen was obtained. An analysis of the material selected for study gave the content—

	Per cent.		Atomic ratios.	
Copper ..	62.50	$62.50 \div 63.4 = 0.986$	4.74	
Iron ..	11.64	$11.64 \div 56 = 0.208$	1.00	
Sulphur ..	25.40	$25.40 \div 32 = 0.794$	3.81	
	99.54			

These results agree fairly well with the requirements of the empirical formula  $\text{Cu}_5\text{FeS}_4$ . The relatively high proportion of iron suggests the presence of a small quantity of chalcocopyrite, which in preparing the sample for study had escaped detection.

#### Experiment with Silver Sulphate Solution.

The finely ground mineral (0.5926 gm.) was digested first on the steam bath for six hours and afterwards at room temperature. After twelve hours the solution was filtered from the insoluble material. From the deposit were obtained 0.5983 gm. of free silver and 0.6037 gm. of combined silver. Traces of copper were present in the residue, which also yielded—

0.0643 gm. iron = 10.85 per cent of the mineral.

0.1478 gm. sulphur = 24.94 per cent of the mineral.

And from the solution were obtained—

0.3615 gm. copper = 61.00 per cent of the mineral.

0.0053 gm. iron = 0.89 per cent of the mineral.

Atomic proportions of the copper dissolved by the silver solution and the iron and sulphur recovered from the residue:—

	Per cent.	
Copper ..	61.00	$61.00 \div 63.4 = 0.962$
Iron ..	10.85	$10.85 \div 56.0 = 0.193$
Sulphur ..	24.94	$24.94 \div 32.0 = 0.780$
and		
	Cu.	Fe. S.
0.962 : 0.193 : 0.780	= 4.98	: 1.0 : 4.04

The results obtained by this chemical reaction approximate the requirements of the empirical formula  $\text{Cu}_5\text{FeS}_4$  more closely than do the results obtained by a gross analysis of the sample.

Atomic proportions of the dissolved copper and the precipitated silver products:—

	Per cent.	
Dissolved copper ..	61.00	$61.00 \div 63.4 = 0.962$
Free silver ..	100.9	$107.9 \div 107.9 = 0.935$
Combined silver ..	101.8	$107.9 \div 107.9 = 0.943$
and		
	Copper.	Free silver. Combined silver.
0.962 : 0.935 : 0.943	= 1.00	: 0.97 : 0.98

This experiment shows that for every atom of copper dissolved by the silver sulphate solution one atom of free silver and one atom of combined silver in the residual material are deposited. It is apparent therefore that the copper of this bornite is cuprous, just as it is in chalcocite, and to express the cuprous nature of the copper it is convenient to use for this bornite the formula  $5\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ , after the dualistic system. This formula may be considered a constitutional formula for the mineral under examination, and its corresponding molecular formula becomes  $\text{Cu}_{10}\text{Fe}_2\text{S}_8$ .

The proportional amounts of the substances participating in this reaction of bornite may therefore be expressed by the equation—



Thus 1 gm. of this bornite is capable of precipitating 2.15 grms. of silver as silver and silver sulphide. In strong contrast with the reactivity of its cuprous constituent is the inertness of the sulphoferric portion of the bornite.

Inasmuch as the group  $\text{Fe}_2\text{S}_3$  is not known to exist as an independent mineral, the formation of a silver ferric sulphide as one of the products of the reaction of bornite with silver sulphate solution may be presumed. Moreover, from the stability of the compound residual products it seems not improbable that in regions abounding in silver deposits associated with bornite some silver sulphoferric mineral as a secondary product may yet be found. It is hoped that further study of the conduct of copper iron sulphide minerals with silver salt solutions will shed light on the chemical relations which sternerbergite and its allied minerals bear to one another.

#### A SIMPLIFIED FERROUS SULPHATE METHOD FOR THE DETERMINATION OF VANADIUM IN STEEL.

By GEORGE T. DOUGHERTY.

IN the application of Johnson's ("Analysis of Special Steels") or similar methods for the determination of vanadium in steel considerable difficulty is often experienced in producing a colourless or "old rose" shade with ferrous sulphate in the solution, containing an excess of permanganate after the preliminary oxidation of the vanadium, and in obtaining consistent results on blank steels and vanadium steels. To obviate this difficulty the following method has been developed, in which this oxidation of the vanadium is effected by a sufficient quantity of nitric acid alone or with ammonium persulphate.

**Method.**—Treat 2 to 4 grms. of the drillings in a 500 cc. Erlenmeyer flask with 60 cc. of water and 10 cc. concentrated sulphuric acid. After heating the solution nearly to boiling until solution is complete, add 40 cc. of nitric acid (sp. gr. 1.20), and boil thoroughly for ten minutes to oxidise the iron and vanadium and to expel the last traces of nitrous fumes. Cool the solution, add 60 cc. of cold sulphuric acid (1:2), and dilute in a 600 cc. beaker to 450 cc. Add 3 cc. of a freshly prepared 1 per cent solution of potassium ferricyanide, and titrate rather rapidly, with constant stirring, with 0.05 N ferrous ammonium sulphate, to the appearance of the first dark blue colour. The end point can best be observed by looking through the side of the beaker toward the bottom of the beaker, placed directly before a window. Deduction of a blank of 0.4 cc. of the ferrous solution has been found necessary, and is independent of the weight of the sample, the presence of chromium, and of the carbon content up to 0.5 per cent C.

For steels with over 0.50 per cent C, the blanks are higher, and, moreover, with 4 gm. samples of such steels, the end point is rendered indistinct by a turbidity which appears toward the end of the titration. This difficulty may be avoided by adding to the solution immediately after the boiling with nitric acid as above 60 cc. of 1:2 sulphuric acid and 5 to 8 grms. of ammonium persulphate (which in the absence of silver nitrate will not oxidise the Cr and Mn), and continuing to boil for fifteen minutes, so that all nitrous oxides and hydrogen peroxide are expelled. (Before this second boiling wash down with hot water loose specks of the persulphate which stick to the glass). Cool, dilute, and titrate as above. After such treatment the blank is 0.35 (instead of 0.4 cc.) for steels with under 0.5 per cent C, and 0.5 cc. for 0.60 to 0.70 C, and 0.6 cc. for 0.90 to 1.25 C steels. The blanks are the same with or without the persulphate treatment for steels of over 0.50 per cent carbon.

The ferrous ammonium sulphate solution may be



standardised against 0.1 N permanganate, the strength of which has been determined with sodium oxalate. The iron value of the permanganate multiplied by 0.917 gives the vanadium value.

By this method the following results were obtained, the chromium in experiments 9, 10, 13, and 14 being added as  $K_2Cr_2O_7$  before the solution of the steel.

The following steels were employed:—

- A—U.S. Bureau of Standard Sample No. 24, containing 0.15 per cent V, 0.35 per cent C, and a trace of Cr.
- B—U.S. Bureau of Standards Sample No. 30, containing 0.21 per cent V, 0.37 per cent C, and 1.35 per cent Cr.
- C—A steel casting, containing 0.215 per cent V, 0.30 per cent C, and no Cr.
- D—A plain steel, containing 0.85 per cent C.
- E—A plain steel, containing 1.25 per cent C.

TABLE A.—Vanadium Determinations by Simplified Method.

Expt.	Sample.	Weight of sample. Grms.	Persulphate added. Grms.	Vanadium found. G.ms.
1	A	2	0	0.148
2	A	4	0	0.146
3	B	2	0	0.206
4	B	4	0	0.208
5	C	2	0	0.216
6	C	4	0	0.216
7	D	2	0	0.222
8	E	2	0	0.210
	E	2		
	E	2	0	0.210
9	D	2		
	1.3 p.c. Cr	2	0	0.200
10	E	2		
	1.3 p.c. Cr	2	7	0.216
11	D	2	7	0.216
	C	2	7	0.216
12	E	2		
	C	2	7	0.216
13	D	2		
	1.3 p.c. Cr	2	7	0.210
14	E	2		
	1.3 p.c. Cr	2		

From these results it is apparent that in general for such materials the method is accurate to 0.1 per cent vanadium.

If chromium also is to be determined, it is determined in a separate portion of the sample, using any of the usual volumetric methods.—*Journal of Industrial and Engineering Chemistry*, vii., No. 5.

## THE SEPARATION OF MAGNESIUM FROM LITHIUM BY MEANS OF AMMONIUM CARBONATE IN ALCOHOLIC SOLUTION.

By J. GRAY DINWIDDIE.

THE following work was undertaken to determine the conditions under which lithium may be separated quantitatively from magnesium by means of ammonium carbonate in alcoholic solution. It has been shown (Gooch and Eddy, *Am. Journ. Sci.*, 1908 [4], xxv., 444) that by the agency of such a solution magnesium may be separated quantitatively from sodium and potassium, and that very small amounts of magnesium may be detected qualitatively in presence of limited amounts (100 mgrm.) of lithium (Noyes and Bray, "A System of Qualitative

Analysis for the Common Elements," *Technology Quarterly*, xxii., 472). In the quantitative procedure the solution containing the salts of magnesium, sodium, and potassium is brought to a volume of about 50 cc., an equal amount of absolute alcohol is added, precipitation is made by addition of 50 cc. of a saturated ammoniacal solution of ammonium carbonate in 50 per cent alcohol, and the mixture is allowed to stand half an hour after stirring vigorously for five minutes. If the amount of alkali salt present is small, the precipitate may be collected without further treatment upon asbestos in the perforated crucible, washed with the precipitant, dried, ignited, and weighed as magnesium oxide. When the amount of alkali salt is large the precipitate may be freed from included alkali salt by decanting the supernatant liquid through the prepared asbestos filter, dissolving the precipitate in hydrochloric acid, and reprecipitating by ammonium magnesium carbonate as at first. This second precipitate, collected upon the filter used in the decantation, leaves upon ignition a practically pure magnesium oxide. The essential condition of this process is that precipitation shall be brought about by a considerable excess of ammonium carbonate in a 50 per cent alcoholic solution.

In the work to be described it was convenient to make use of 93 per cent alcohol instead of absolute alcohol in making up the solution to be treated and the precipitant, but the proportions of solution and precipitant were so adjusted that the liquid at the time of precipitation should be 50 per cent alcohol.

The alcoholic solution of ammonium carbonate was made by mixing 1500 cc. of the saturated aqueous solution of that reagent with 360 cc. of concentrated ammonium hydroxide and 1900 cc. of 93 per cent alcohol, settling out the precipitated ammonium carbonate and filtering off the clear solution. In carrying out the determinations, portions of the magnesium chloride solution (15 to 20 cc.) were measured out and carefully weighed, lithium chloride was introduced in the amounts stated, 25 cc. of 93 per cent alcohol and 50 cc. of the precipitating mixture were added, the mixture was stirred vigorously (for perhaps a minute) and set aside for five hours or more. The supernatant liquid was decanted upon asbestos in the perforated crucible (weighed), the precipitate was stirred up with more of the precipitating mixture and allowed to settle, and the liquid was again decanted upon the same asbestos filter. In the cases in which a single precipitation was employed the precipitate was simply transferred to the filter and washed with the precipitating mixture, and ignited to constant weight. When two precipitations were made in order to remove possible inclusions of lithium salt from the precipitated ammonium magnesium carbonate, the precipitate was dissolved in the least necessary amount of hydrochloric acid, the solution was diluted to a volume of 10 cc., 13 to 15 cc. of 93 per cent alcohol and 50 cc. of the precipitant were added, and the precipitate was transferred, washed, and ignited as described.

Tables I. and II. show the results obtained with solutions of magnesium chloride with and without the addition of lithium chloride in varying amount. The mean of the three determinations in which the solution contained no lithium salt was taken to fix the value of the magnesium solution, and by comparison with this standard the errors of the single determinations were computed.

It will be seen that while the separation of 0.2 gm. of magnesium oxide from lithium amounting to 0.5 gm. of the chloride, or 0.083 gm. of the element, may be reasonably good in a single precipitation, the ammonium magnesium carbonate only once precipitated is largely contaminated, presumably with lithium carbonate, when the amounts of lithium are considerably greater. Two precipitations made in the manner described will yield, however, a very fair separation of the magnesium (about 0.3 gm. of the oxide) from lithium chloride equivalent to 0.2 gm. to 0.3 gm. of the element.

TABLE I.—Standardisation of the Magnesium Solution.

Solution MgCl <sub>2</sub> Gms.	MgO found Gm.	MgO found per gram. of solution. Gm.
20.4071	0.2788	0.013662 (a)
20.3956	0.2779	0.013626 (a)
15.4271	0.2108	0.013664 (b)

Average . . . 0.013651

(a) One precipitation.

(b) Two precipitations; washings made with precipitant saturated with precipitate.

TABLE II.—Separation of Magnesium from Lithium.

Solution of MgCl <sub>2</sub> Gms.	LiCl=Li taken.		MgO taken. Gm.	MgO found. Gm.	Error. Gm.	No. of precipita- tions.
	Gm.	Gm.				
14.8191	0.5	0.083	0.2023	0.2028	+0.0005	1
15.1409	1.0	0.166	0.2067	0.3191	+0.1124	1
20.7421	0.5	0.083	0.2831	0.2834	+0.0003	2
20.1706	0.5	0.083	0.2753	0.2761	+0.0008	2
19.9744	1.25	0.207	0.2727	0.2730	+0.0003	2
20.3998	1.25	0.207	0.2785	0.2783	-0.0001	2
19.9291	2.10	0.347	0.2718	0.2730	+0.0012	2

The author wishes to thank Prof. Gooch for advice and assistance in carrying out the above work.—*American Journal of Science*, xxxix., No. 234.

## THE MANUFACTURE OF ACID PHOSPHATE.\*

By WM. H. WAGGAMAN, Scientist in Fertiliser Investigations.

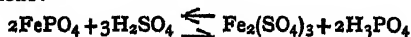
(Continued from p. 299).

## IMPURITIES IN PHOSPHATE ROCK (continued).

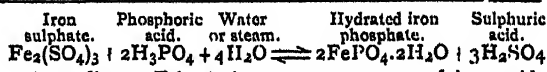
## Compounds of Iron and Aluminium.

IRON and aluminium oxides, either in the free state or combined as phosphates, are the most objectionable of the impurities found in phosphate rock. These substances even when present in very small quantities cause a certain amount of "reversion" in the superphosphate, and when present in large quantities are likely to produce a sticky acid phosphate unfit for commercial purposes.

The phosphate of iron in natural occurrences may conveniently be represented by the formula  $\text{FePO}_4$ , although actually it is probably of an indefinite composition. The exact reactions that take place when this substance is treated with sulphuric acid are not known. Unquestionably, however, the iron is distributed between the two acids. A mixture of "sticky" disagreeable physical properties results, the composition of the solid part of the mixture changing with the composition of the liquid part which is formed at the same time. Both the solid and the liquid contain all three constituents—iron, sulphuric acid, and phosphoric acid. Dilution of this liquid mass by the addition of water causes a precipitation of more jelly-like material containing relatively more iron and phosphoric acid than sulphuric acid. The general course of the reactions are sufficiently well known to justify the assumption that they go mainly according to the following equations:—

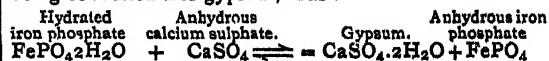


But a part of the iron sulphate produced reacts with the phosphoric acid or monocalcium phosphate in the mass forming hydrated phosphate of iron, the gelatinous precipitate almost insoluble in water, and when present in any quantity causing the acid phosphate to be sticky and difficult to handle. The reactions may be represented thus:—



According to Fritsch, however, 2 per cent of iron oxide in the raw material is not objectionable, because the quantity of iron sulphate produced therefrom remains unaltered in the superphosphate ("Manufacture of Chemical Manures," 1911, p. 78). It is true that in properly made acid phosphate nearly all of the phosphoric acid is soluble in water even though there is sufficient iron present to cause part of it to revert, but Fritsch is probably in error in attributing this to the fact that the iron is all in the form of sulphate. Schneider (*Zeit. Anorg. Chem.*, 1894, v., 84; vii., 386) has shown experimentally that solutions of sulphate of iron increase the solubility of iron phosphate, and Cameron and Bell have demonstrated that gypsum, lime, and phosphoric acid also increase the solubility of this substance (*Bull. 41*, Bureau of Soils, U.S. Dept. Agr., 1907).

Hydrated iron phosphate may be converted into the anhydrous and less soluble condition by reacting with anhydrous calcium sulphate; the last-named compound being converted into gypsum, thus:—



This last reaction partly explains why acid phosphate in excellent mechanical condition, but with a relatively high percentage of phosphoric acid insoluble in water, is often made from rock containing large quantities of iron and aluminium.

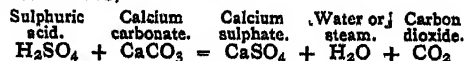
Compounds of aluminium react in a manner similar to those of iron, but to a less marked degree.

Fertiliser manufacturers and authorities differ widely on the question of what constitutes the maximum quantity of iron and alumina that a phosphate rock can contain and still be useful in the manufacture of acid phosphate. Wyatt says that phosphates containing from 6 to 8 per cent of iron and alumina may be used, provided there is sufficient carbonate of lime present to produce a dry pulverulent mass ("Phosphates of America," 1891, p. 111). Schuchert ("Die Fabrikation des Superphosphates," 1909, p. 79) and Fritsch ("Manufacture of Chemical Manures," 1911, p. 78) are inclined to consider any quantity of iron and alumina in excess of 3 per cent as undesirable. Stillwell states that phosphates containing from 4 to 6 per cent of these oxides can be handled, but the presence of more than 2 per cent is objectionable ("Industrial Chemistry," 1912, p. 103).

Thousands of tons of high-grade acid phosphate, however, are now annually made from Tennessee brown rock phosphate containing as high as 5 per cent of the combined oxides of iron and aluminium, and though the handling of such phosphates necessitates an increased consumption of sulphuric acid, there seems little reason why they should not be used in making acid phosphate, provided they are so manipulated that a dry readily workable product is obtained.

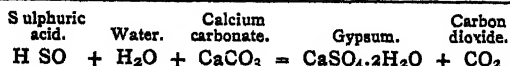
## Carbonates of Lime and Magnesia.

Carbonates are frequently very desirable impurities in phosphate rock, provided they do not occur in quantities so great that the percentage of phosphoric acid present is materially reduced. The carbonic acid is usually combined with lime, and it is in this form that it is considered here. Sulphuric acid acts upon calcium carbonate to form calcium sulphate, water or steam, and carbon dioxide, which escapes as a gas. The reaction may be represented thus:—



If sufficiently diluted sulphuric acid is used the excess of water combines with the calcium sulphate to form gypsum. Modifying the above equation, therefore, we obtain:—

\* Bulletin 144, U.S. Department of Agriculture, Bureau of Soils.



The advantages of having small quantities (and in some cases large quantities) of carbonate of lime present in phosphate rock are threefold:—First, the heat evolved in the reaction between carbonates and sulphuric acid is sufficient to warm the pasty mass of acid and phosphate rock, and thus promote chemical action between these more slowly reacting substances; second, the escape of carbon dioxide from the mass renders the acid phosphate porous and more readily dried; and third, the gypsum formed prevents the formation of the gelatinous iron and aluminium compounds, and thus helps render the product dry and in good condition for distributing or mixing with other fertilising ingredients.

#### REVERSION OF SUPERPHOSPHATE.

The reversion of superphosphate, as the term implies, originally meant the return of the phosphoric acid to a condition insoluble (or nearly so) in water. In reality the expression "reverted" phosphoric acid is now wrongly used in a much broader sense, and includes all of the phosphoric acid of superphosphate which is soluble in certain citrate solutions. In this paper, however, reverted phosphoric acid is used in the strict sense of the word.

When a superphosphate is allowed to stand and take up water from moist air, as it sometimes does while in storage; or is diluted by the soil water when it is applied to the soil; or is added to an excess of water, as is done in the laboratory before commencing analytical operations, then, in any one and in all of these cases, less soluble compounds of phosphoric acid are formed. If compounds of iron and aluminium are present the formation of phosphates insoluble in water is much more marked. This general process is known as *reversion*, and the superphosphate is said to have *reverted*, and the product is called *reverted phosphate*. The theory of this reversion is now clearly understood, owing to the investigations in this country of Cameron and Bell (*Bull.* 41, Bureau of Soils, U.S. Dept. Agr., 1907) and Seidell (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1503), and of Bassett in England (*CHEMICAL NEWS*, 1907, xcv., 21; *Zeit. Anorg. Chem.*, 1907, liii., 34), who have shown that certain concentrations of phosphoric acid or of other acids must exist in the water in contact with a calcium or iron phosphate for the solid definite "acid" compounds to be stable. Dilution of the acid liquor causes the solids to decompose into more basic and less soluble compounds. While the theory of these phenomena has been made clear only recently, the main facts have long been known, and as is so commonly the case, certain popular misconceptions have held sway long enough to become regarded as facts even by many well-trained chemists. Thus, it is popularly held that monocalcium phosphate is soluble in water, but dicalcium phosphate is not; dicalcium phosphate is in turn soluble in certain citrate solutions, while tricalcium phosphate is not, and on these supposed facts methods for separating the three compounds have been suggested. Moreover, it is held that while the water-soluble monocalcium phosphate and citrate soluble dicalcium phosphate are "available" to plants, more basic phosphates are not.

The facts are that the presence of citric acid or ammonium citrate in the water does increase the solubility of the phosphates of lime, iron, and alumina, and it has been shown by field tests that phosphates soluble in such solutions are more quickly active under soil conditions than those which do not dissolve in the same mediums. Hence a convenient control or "police" method of analysing commercial fertiliser containing phosphates has been developed. But the "citrate solubility" gives no definite information about the constitution of the phosphate. The actual phenomena involved in *reversion* can be best followed by the microscope.

Reversion is, however, a reality, and one to be carefully avoided. The reverted phosphate is frequently difficult to handle, and even if its mechanical condition is good and the phosphoric acid present is classed as available according to the official method of analysis, many consumers seriously object to its use because the percentage of water soluble phosphoric acid present is relatively low. Moreover, reverted phosphate is not easily susceptible to re-treatment in the factory, and usually the manufacturer can better afford to throw it away than attempt to work it over in competition with untreated raw rock.

#### METHOD OF MANUFACTURE.

##### *Grinding the Rock.*

The phosphate rock is first put through a crusher and broken in pieces not larger than a walnut. This crushing is hardly necessary in the case of Florida pebble phosphate or the screenings from the hard rock phosphate, since the pebbles and fragments are usually small enough to be fed directly to the mill.

The pulverisers for phosphate rock that are probably most widely used in this country are those of the roller type, in which the material is crushed by steel rollers revolving within a steel ring. Sometimes the ring within which these rollers revolve is rigid and the power is transmitted through the rollers. In another form of mill, the ring is revolved by a shaft, and the rollers are revolved in turn by the ring.

There are a number of different makes of these pulverisers, but space does not permit a detailed explanation of their construction. For convenience they all may be placed in one of two broad classes, namely, the type which combines both grinding machinery and screens in one, and the type which discharges the partly ground material into elevators to be subsequently screened or separated, the coarser material being returned to the mill for further grinding.

Mills of the first type occupy but little space, do not require auxiliary screens and conveyors, and the grinding is all finished in one operation. The fact, however, that the pulverised phosphate is not separated from the coarser rock until forced through the screens within the mill cuts down somewhat the efficiency of this type of machine, since considerable space and power is always taken up by material already ground. Another disadvantage of this type of mill is that any clogging of the screens or break in the same necessitates the shutting down of the entire mill while the damage is repaired. The manufacturers of the other type of mill claim to have overcome these disadvantages in their machines; the ground material is continually discharged from the mill and separated from the coarser rock by passing through revolving or over vibrating screens. Any trouble with a screen can be corrected without stopping the mill by simply cutting off the supply of rock to that screen. Since the material flows over the screens instead of being forced against them as in the case of the other type of mill, the repairs necessary on the screens are reduced to a minimum. This type of mill, however, with its auxiliary screens and conveyors, takes up considerable space, costs more to install, and requires a greater amount of supervision.

The amount of material which can be pulverised per hour depends on the size of the mill, the character of the phosphate rock used, and the degree of fineness to which it is ground. A mill of the size usually employed in fertiliser factories may grind from 10 to 12 tons per hour of Tennessee brown rock phosphate to pass a 60-mesh sieve, but this mill will probably not grind more than 7 or 8 tons of pebble phosphate to the same degree of fineness in that period of time.

A very ingenious ball mill is that of Pfeiffer (German patent No. 116,195). The grinding is done by means of steel balls or flint pebbles, and the separation of the fine material from the coarse is effected by means of a current of air. All loss of time due to the clogging and repairing of screens is thus avoided, and a product of any degree of

TABLE III.—Weight of "Chamber Acid" of various Strengths required to convert One Pound of each of the Ingredients of Phosphate Rock into Soluble Compounds.

Material acidulated—Ingredient.	Quantity and strength of acid required.							
	48° B.	49° B.	50° B.	51° B.	52° B.	53° B.	54° B.	55° B.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ .. ..	1.060	1.040	0.916	0.992	0.970	0.918	0.927	0.907
Calcium fluoride, $\text{CaF}_2$ .. ..	2.117	2.067	2.019	1.972	1.928	1.885	1.843	1.803
Iron phosphate, $\text{FePO}_4$ .. ..	1.640	1.601	1.564	1.528	1.494	1.460	1.428	1.397
Aluminium phosphate, $\text{AlPO}_4$ .. ..	2.023	1.975	1.929	1.885	1.842	1.801	1.761	1.723
Calcium carbonate, $\text{CaCO}_3$ .. ..	1.652	1.613	1.576	1.539	1.504	1.471	1.438	1.407

fineness can be obtained by simply regulating the strength of the air current.

The degree of fineness to which phosphate rock is ground often has a very important effect on the acid phosphate produced therefrom. Phosphate rocks low in carbonates and high in iron and aluminium are but slowly acted upon by sulphuric acid, and should therefore be ground very fine. Phosphates containing large quantities of carbonate of lime are acted upon quite rapidly, and consequently do not require extremely fine grinding. In ordinary practice the rock is usually ground so that 80 to 90 per cent will pass a 60-mesh sieve, but in working with less soluble phosphates it is frequently desirable to grind them so that 80 to 85 per cent will pass an 80-mesh sieve.

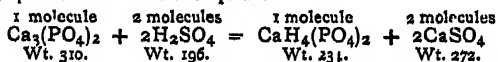
#### Quantity, Strength, and Temperature of Sulphuric Acid.

The quantity and strength of sulphuric acid which should be used in treating phosphate rock is a perplexing problem, yet many manufacturers give it little consideration, proceeding in a "rule of thumb" manner without regard to the composition of the rock. The reason why many of these latter obtain such good results may be explained by the fact that they have been using one grade of rock for years, and have thus learned by actual experience the proper proportions of acid and rock to use. A sudden change in the composition and grade of the phosphates often results in a loss of both acid and rock in attempts to find the quantity of acid required for this new material. While actual trial mixings should be made when testing out a new grade of phosphate, these tests should be intelligently conducted with due regard to the composition of this rock. Take, for example, a sample of high-grade Florida hard rock phosphate having the following composition:—

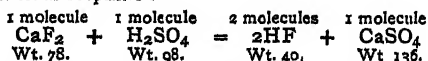
	Per cent.
Moisture .. ..	0.5
Calcium fluoride, $\text{CaF}_2$ .. ..	4.5
Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ .. ..	80.0
Calcium carbonate, $\text{CaCO}_3$ .. ..	3.5
Aluminium phosphate, $\text{AlPO}_4$ .. ..	6.0
Silica $\text{SiO}_2$ .. ..	5.5
Total .. ..	100.0

The problem is to convert the phosphoric acid of this rock into a soluble form and yet obtain a dry product which can be uniformly spread on the soil or readily mixed with other ingredients to make up a complete fertiliser. The reactions which are desired may be represented in their simplest form, thus:—

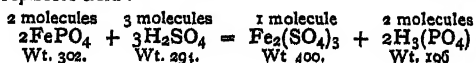
1. Conversion of tricalcium phosphate to monocalcium phosphate and calcium sulphate:—



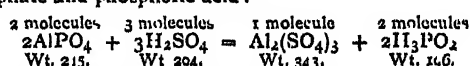
2. Conversion of calcium fluoride to hydrofluoric acid and calcium sulphate:—



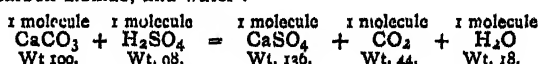
3. Conversion of iron phosphate to iron sulphate and phosphoric acid:—



4. Conversion of aluminium phosphate to aluminium sulphate and phosphoric acid:—



5. Conversion of calcium carbonate to calcium sulphate, carbon dioxide, and water:—



If 196 parts by weight of sulphuric acid are required to convert 310 parts of tricalcium phosphate into monocalcium or soluble phosphate, then 0.632 part of acid will be required for every 1 part of tricalcium phosphate. If we use ordinary "chamber acid" of 50° B. strength which contains, according to the table on p. 298, 62.18 per cent of sulphuric acid, 1.016 parts will be necessary for every 1 part of tricalcium phosphate.

In Table III., modified from one prepared by Wyatt ("Phosphates of America"), is given the quantity of sulphuric acid of various strengths necessary to bring about the reactions outlined above.

Table IV. gives the quantities of sulphuric acid of various strengths required for every 100 pounds of the phosphate rock.

TABLE IV.—Quantities of "Chamber Acid" required (theoretically) to Convert 100 Pounds of Florida Hard Rock Phosphate into Acid Phosphate.

Components of rock.	Per cent.	Strength and quantities of acid required for 100 pounds of rock.				
		48° B.	50° B.	52° B.	54° B.	55° B.
		Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ .. ..	80.0	84.8	81.3	77.6	74.1	71.1
Calcium fluoride, $\text{CaF}_2$ .. ..	4.5	9.5	9.1	8.7	8.3	8.0
Iron phosphate, $\text{FePO}_4$ .. ..	—	—	—	—	—	—
Aluminium phosphate, $\text{AlPO}_4$ .. ..	6.0	12.1	11.6	11.1	10.6	10.2
Calcium carbonate, $\text{CaCO}_3$ .. ..	3.5	5.8	5.5	5.3	5.0	4.8
Silica, $\text{SiO}_2$ .. ..	5.5	—	—	—	—	—
Moisture, $\text{H}_2\text{O}$ .. ..	0.5	—	—	—	—	—
Total .. ..	—	112.2	107.5	102.7	98.0	94.1

It has been found, however, that the quantity of sulphuric acid theoretically required to convert phosphate rock into acid phosphate does not always produce the best results. The physical condition of the acid phosphate is just as important as its chemical composition, and sometimes the proper mechanical condition cannot be obtained except by sacrificing some of the water soluble phosphate. In factory practice it is often well, therefore, to add a little less sulphuric acid than is necessary to satisfy the equations outlined above.

The strength of sulphuric used is another detail of great importance in the production of acid phosphate. The quantity of strong acid sufficient to bring about the desired chemical reactions is of such small bulk and has such a viscosity that it is difficult to obtain an intimate mixture with the ground phosphate; moreover, the calcium sulphate produced, being much less soluble in strong than in

weak sulphuric acid (*Bull.* 33, Bureau of Soils, U.S. Dept. of Agr., 1906, p. 41), forms a relatively insoluble coating over the phosphate, preventing further action by the acid.

On the other hand, if very dilute acid is employed, the amount required to bring about the necessary chemical reactions is so great and so much water is contained therein that it is almost impossible to obtain a product in good mechanical condition. The strength of acid with which the best results are ordinarily obtained ranges from 50° to 55° B., though phosphates very high in iron and aluminium compounds sometimes yield better to slightly stronger acid.

There is considerable difference of opinion concerning the temperature at which sulphuric acid should be added to phosphate rock. Some manufacturers, however, give little heed to this important point, mixing their acid and rock in the same proportions winter and summer at whatever temperature the air happens to be. Others believe in heating the acid to 50° to 55° C. before using, while many others claim it is bad practice to use acid at a temperature below 25° or above 30° C.

It is obvious that this matter should not be disregarded entirely, for in mixing acid and rock either very low or excessively high temperature may seriously affect the product. No definite rule, however, can be prescribed, for here, again, the composition of the phosphate used is the controlling factor.

Phosphates containing large quantities of carbonates heat up rapidly when mixed with sulphuric acid. If the mixture becomes very hot violent frothing occurs, and the mass is apt to overflow from the pan. Rocks of this type should not be treated with hot acid. When dealing with phosphates high in compounds of iron and aluminium, however, it often saves time to use acid heated to a temperature of 50° to 55° C. The reactions then begin promptly in the pan, and the mixture can be dumped without fear of its cooling before the final chemical changes take place.

#### *Mixing the Acid and Rock.*

When the manufacture of acid phosphate was first suggested by Liebig, and for many years afterwards, the mixing process was all done by hand. Certain proportions of acid and rock were dumped into shallow open pits or troughs, and worked with hoes in a manner similar to that in which mortar is mixed. The material was then allowed to stand in the pit until the chemical reactions were complete and the superphosphate dry enough to be dug out. The modern factory process has almost entirely displaced this pioneer method of making acid phosphate. Machines are now employed which are capable of mixing efficiently, in two to five minutes, quantities of rock and acid weighing from 1 to 2 tons.

There are several types of mixers or acidulators used in this country, and the following general description applies to almost all of those ordinarily employed:—A cast-iron revolving pan from 4 to 8 feet in diameter and from 1 to 2 feet deep is driven by pinions. The pan is equipped with either one or two agitators or stirring devices which consist of heavy iron spiders having four arms fitted with steel ploughs. These stirrers are driven by bevel gears. In the centre of the pan is the discharge hole, which is closed by a valve operated by a lever. This same lever also controls a scraper which is lowered into the pan as the plug is raised.

The weighed charges of acid and rock are run into the revolving acidulator at the same time, and stirred for at least two minutes, or until an intimate mixture is obtained. The lever which controls the scraper and discharge valve is then lowered, and the material ejected into the "den" directly below, or into a car which hauls it to the storage shed and dumps it on a pile.

Both the "den" and "open dump" systems of making acid phosphate are employed in this country. Each has points to recommend it and each has certain objectionable features.

(To be continued).

#### SOFT SODA GLASS, SUITABLE FOR X-RAY BULBS.

THE Glass Research Committee of the Institute of Chemistry find that a glass such as that made from formula No. 10, recently published by them and recommended for X-ray bulbs, does not give a green phosphorescent glow if it is made from approximately pure materials. The slight glow given is blue. In view of the fact that a green phosphorescence appears to be preferred by users of X-ray tubes, it seemed desirable to determine the conditions for obtaining this effect. It has been traced to the presence of manganese, and such a glass as No. 10 will give this green glow if manganese dioxide is added to the batch mixture in the quantities frequently used to correct the colour due to iron.

#### A WAKE-UP IN INORGANIC CHEMISTRY NEEDED.

A CORRESPONDENT who has devoted much attention to this subject writes as follows:—

"It has always seemed highly probable that *potassium* salts must exist under the vast salt deposits in Durham, Cheshire, &c. Lithium salts are, I believe, entirely obtained from Germany and America, from lepidolite, petalite, &c., while in the hot spring at the Wheal Clifford Mine in Cornwall 800 lbs. of lithium chloride are running to waste every twenty-four hours! (*CHEMICAL NEWS*, x., 181). Enormous amounts of barium salts are imported from Germany, while the English sources are neglected (of barium sulphate at least). Strontium carbonate is imported from Westphalia, while the mines at Strontian, Argyllshire, lie idle. Some of the old miners there told me some years ago that there were great quantities of strontium carbonate in the mines, but underneath the top layers of calcite."

This could be extended to many other minerals. We shall be pleased to receive comments and letters discussing the points here raised.

#### WELSH NOTES.

(By Our Special Correspondent).

BUSINESS at Swansea Docks during the past week was very satisfactory, notwithstanding increased restrictions, and on totalling the tonnage for the week we find an increase compared with the total of the previous week of 15,000 tons, whilst strangely enough the figures for the corresponding period in last year are identical. Whilst exports were brisk the import trade was under the average. Chief among the imports were 1280 tons iron ore from France, 1227 tons steel scrap, and 1700 tons pig-iron from Italy, 1860 tons calamine from Spain. Patent fuel exports amounted to 19,220 tons. Shipments of tinplates totalled 69,733 boxes, 87,231 boxes being received from works. Stocks in the dock warehouses and vans amounted to 312,856 boxes, compared with 295,358 boxes the previous week and 232,179 boxes the corresponding week last year.

The shipping trade at Port Talbot docks was exceptionally brisk last week, registering an increase of 10,000 tons over the corresponding week in last year. A feature of the imports was two very large cargoes of steel billets and pig-iron. Patent fuel exports totalled 4470 tons.

Trade was very active in all departments of the Swansea Valley with the exception of the tinplate works, where the average production represented big decreases. The position at the blast-furnace was still pressing, and there was a substantial increase in the production of pig-iron. All



steelworks were in full swing, and copper works were active. Employment at the spelter factories continued very heavy. Lead-piping and safety-fuse factories experienced a brisk time, and there was an increase in the demand for material. A brighter outlook was observed in the sulphuric acid factories. The position of the Mond Nickel Works and the Mannesmann Tube Works showed increasing pressure, whilst iron and brass foundries continued active.

Dowlais Steel and Iron Works experienced another very brisk week. The Goat Mill sent out a very good tonnage of heavy steel rails, steel sleepers, square bars, cogging billets, tin bar, &c. The Big Mill was kept at the making of sole plates, fish plates, and tram-rails of short lengths. The despatching was done expeditiously, and no time was lost.

The Caerleon Engineering and Tinplate Works, which have been closed for about two years, are to be re-started on Monday, June 21, as tinplate works only. Mr. John Paton, of Pontypool, who has similar works in the eastern valleys of Monmouthshire, is the new proprietor. It is estimated that employment will be found for 170 to 200 men and girls. Two mills of the Ely Tin Works, Pontyclun, are also being started this week by Messrs. Richard Thomas and Co.

The official return of tonnage dealt with at the Swansea Docks for the month of May contains some interesting information. As was only to be expected there has been a falling off in the exports of coal, coke, and tinplates; tin, terne, and black plates dropping from 35,590 in May last year to 26,149 tons. Against this there has been an increase in the export of patent fuel from 71,312 tons in May last year to 77,753 tons in May this year. Regarding the imports we find that there has been a big increase in zinc and iron-ore. In May, 1914, the imports of zinc-ore and alloys was 3038 tons, whereas last month it was 12,073 tons, while 11,060 tons of iron-ore was imported last month against 4150 tons in the corresponding month of last year.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, June 3, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

*"On the Shapes of the Equipotential Surfaces in the Air near Long Buildings or Walls, and on their Effect on the Measurement of Atmospheric Potential Gradients."* By Prof. C. H. LEES, F.R.S.

The shapes of the equipotential surfaces are determined and the equipotential lines drawn to scale in the following cases:—

1. A thin vertical wall.
2. A retaining wall separating a lower from a higher horizontal plane.
3. A series of equidistant parallel vertical walls.

In each case the normal vertical potential gradient may be calculated from observations of the potential at any point. A point on each wall is indicated at which the horizontal potential gradient is identical with the normal vertical gradient.

*"The Influence of Gases on the Emission of Electrons and Ions from Hot Metals."* By Prof. O. W. RICHARDSON, F.R.S.

As is well known, the thermionic saturation current  $i$  is expressed accurately and quite generally over wide ranges of temperature by the equation—

$$i = AT^{\frac{1}{2}}e^{-b/T},$$

In the case of metals in particular, the equation is satisfied when the metals are contaminated by the presence of a gaseous atmosphere, as well as when the surfaces of the pure metals are tested. In general, however, the effect of the contaminating gas is to cause large changes in the values of the constants  $A$  and  $b$ .

The changes which are thus brought about in these constants are considered in the present paper. So far as it may be considered reliable, the available evidence shows that  $A$  and  $b$  for a given metal always change together in such a way that the change in  $\log A$  is proportional to the change in  $b$ . This linear relation is very closely satisfied by the results of all Langmuir's observations with tungsten, for which substance different gases change  $A$  by as large a factor as  $10^{1.2}$ . A similar relation, with an almost equal coefficient of proportionality, is required by the best observations on the negative emission from platinum. In the case of tungsten, contaminants show an increase in  $A$  and  $b$ , whereas with platinum a diminution occurs. All the known data point to the existence of a similar law governing the steady emission of positive ions from platinum.

By applying thermodynamic considerations to the emission of electrons from contaminated surfaces, it is shown to follow from the linear relation between  $\log A$  and  $b$  that the contact potential difference between the pure and the contaminated metal is of the form  $a_0(x - \alpha T)$ , where the constant  $a_0$  has opposite signs for tungsten and platinum, and  $\alpha$  has approximately the same value for both metals.  $T$  is the absolute temperature.

*"The Band Spectrum associated with Helium."* By J. W. NICHOLSON.

Fowler has concluded recently that the heads of the bands in the new spectrum associated with and perhaps due to helium follow laws of the type hitherto peculiar to line-series. A further examination of some points which were in doubt has been made, with the following results:—

1. The paper supports the conclusion that the heads of the bands in the spectrum of Goldstein and Curtis follow ordinary series laws by showing that the doublet separations actually tend to zero at the limits of the series.
2. Both the doublet series isolated by Fowler are strictly analogous to principal series in line-spectra.
3. The generalised Rydberg formula, in which the wave number is a function of  $m + \eta$ , gives the most suitable representation of these series as well as of line-series.

*"The Chromosome Cycle in Coccidia and Gregarines."* By C. DOBELL and A. P. JAMESON.

### PHYSICAL SOCIETY.

Ordinary Meeting, June 11, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER on *"The Coefficient of Expansion of Sodium,"* by E. A. GRIFFITHS and E. GRIFFITHS, M.Sc., was read by the latter.

The thermal expansion and increase in volume on liquefaction of sodium were determined by a method based on the following principle:—

The difference in expansion of a volume of sodium and an equal volume of glass (or quartz) was measured by differential weighing under oil at various temperatures.

A volume of about 250 cc. of sodium was suspended from one arm of a short beam balance and a weighed glass bulb of equal displacement from the other arm.

The experiments show that sodium expands quite uniformly with the temperature up to its melting point.

The value 0.000226 was deduced for the coefficient of expansion. In changing from the solid to the liquid state, an increase of 2.57 per cent occurs in the volume.

# DISCUSSION.

Mr. F. E. SMITH expressed his admiration for the method employed and for the order of accuracy with which the observations appeared to have been made. Would it have been possible to obtain sufficient accuracy with the sodium in an ordinary dilatometer, the remainder of which contained oil, as was often done in the case of other metals?

Mr. A. CAMPBELL asked if there had been no trouble from convection in the oil at the higher temperatures. Had the authors noticed any hysteresis effect in the expansion of the glass globe such as the behaviour of a thermometer bulb would lead one to expect?

Dr. C. CHREE stated that the two curves which Mr. Griffiths had drawn on the board representing the theoretical and experimental results were very similar in form, which might indicate that the theory had something in its favour. Had the coefficient of elasticity been determined for the actual specimen used, or were general results assumed? He believed that the elasticity varied considerably in different specimens.

Mr. J. GUILD asked what precautions had been found necessary to avoid difficulties due to the very uncertain capillary effects where the suspensions enter the oil. Was the compensating bulb evacuated? If it contained air at atmospheric pressure when cold, the pressure would increase by about a third of an atmosphere at 100° C., which would produce an appreciable alteration in the volume of the compensator. The neglect of a correction for this pressure effect would be to give less than the true value for the expansion of the sodium. He had not had time to see whether this would diminish or increase the discrepancy between the observed and theoretical values of  $C_v$ , but it seemed advisable in future work either to evacuate the compensator or to determine its total expansion from all causes by a blank experiment.

Mr. S. D. CHALMERS asked if a check was made to see if the volume of the bulb was the same before and after the experiments. Had the authors tried if Lindemann's formula would agree with their results?

Mr. GRIFFITHS, in reply, said that in the dilatometer method the difference in expansion of sodium and oil would be measured. The coefficient of expansion of oil is about ten times that of a metal, and would have to be determined with considerable accuracy. The method described was intended to measure the expansion relative to that of fused quartz, of which the coefficient is about  $1/200$  that of a metal and is accurately known. The expansion of the oil only affects the ratio of the densities at the two temperatures. The effect of convection was greatly reduced by the symmetrical disposition and closeness of the bulbs. No secular changes were found, the results obtained before and after heating to the higher temperatures agreeing (see Table I. and Fig. 2). With quartz bulbs no secular effects would be possible. The formulæ of Einstein and Debye were able to represent the general form of the atomic heat-temperature curve, but systematic divergences from the experimental results occur and the theories fail to account for the abnormal increase near the melting point. Nernst and Lindemann's formulæ gave a curve very similar to Debye's (see *Phil. Trans. R.S., A*, 1914, ccxiv., 343). He had assumed Richards' value for the elasticity. The suspensions were of fine tinned steel wire. As the oil wetted the surface the capillary effect would probably be constant, and the same for both wires. The compensator was heated to about 200° C. when sealing off and, being stout walled, would be little affected by the changes of pressure of the residual air when heated. The expansion of the compensator was checked by weighing it alone in water at different temperatures.

A paper, entitled "*Notes on the Calculation of Thin Objectives*," was read by Mr. T. SMITH, B.A.

Lens systems which are symmetrical about an axis have in general six degrees of freedom for first order aberrations.

Thin systems have only three degrees of freedom, and in consequence of the limited range of glasses only two degrees of freedom are practically available. In achromatic combinations of two lenses these two degrees of freedom are controlled by the general shape as distinct from the total power of each lens. In general when two given conditions are satisfied the curvatures of the inner surfaces are not equal, so that a cemented combination of two lenses is not possible. Owing to the increased light transmitting powers it is often necessary to have only two glass air surfaces, and thus more than two component lenses are necessary. The effect of bending any thin system as a whole by increasing the curvature of each surface by the same amount is investigated, and it is shown that with two given kinds of glass a triple cemented lens can be formed satisfying two arbitrary aberration conditions. The problem reduces to the solution of quadratic equations, and in general there are four solutions. Illustrations are given of astronomical objectives of both double uncemented and triple cemented forms, and the glasses are determined for which a doublet can be cemented.

# DISCUSSION.

Mr. S. D. CHALMERS expressed his appreciation of the paper. One could get a rapid survey from it of the results which were possible. The special problem of a lens corrected for spherical aberration and coma had been discussed by Harting and also by Von Hoegh. The latter had solved the problem on lines which seemed to him rather simpler to use. He did not quite agree with the author's statement that the use of phosphate crowns had been entirely discontinued. Glasses very like these have been used fairly frequently, especially by Continental makers. There were cases where in computing a lens it was not desired to achromatise completely; where, for example, after correcting for spherical aberration and coma, some residual chromatic aberration was desirable to neutralise the chromatic aberration of the prisms in binoculars.

Mr. A. CAMPBELL asked if the small thickness of the cement used in cemented lenses made an appreciable difference, and if its refractive properties entered into the calculations. What was the range of refractive index available in the modern optical glasses?

The AUTHOR, in reply, was surprised to hear that phosphate glasses were still employed in any case in which they could possibly be avoided. The cement used was always Canada balsam and was entirely neglected in all computations. A range of refractive index of 1.47 to 1.79 was available, but the extreme values were rarely used, 1.49 to about 1.65 or so being the range usually utilised.

A paper "*On Tracing Rays through an Optical System*" was read by Mr. T. SMITH, B.A.

Trigonometrical formulæ have been used for tracing rays not lying entirely in one plane through optical systems, as these can readily be arranged in a form suitable for logarithmic calculation. When a calculating machine is available such computations can be carried out more expeditiously by using algebraic formulæ given in the paper; in form these exactly correspond with the expressions for paraxial rays, and a comparison of the numerical result appears likely to suggest what alterations should be made when a general ray does not behave as desired. It is pointed out that if the two points in which a general ray meets an axial plane are defined as conjugate points, all pairs of conjugate points on a ray are connected by the same relations as hold for object and image points for paraxial rays, and the theory for paraxial rays can be extended to rays in general by placing a suitable interpretation on magnification, &c. The definition of conjugate points can be extended to include rays lying in axial planes, in which case the one point marks the intersection of the ray with the radial focal line formed by rays passing through its conjugate.

## DISCUSSION.

Mr. S. D. CHALMERS was particularly interested in the method of tracing rays through a system. The relations between the various quantities involved was of considerable interest. The author's methods of treatment seem to present many possibilities in addition to the cases actually quoted. By extending them he may simplify very considerably many important computations. Some time ago he had used somewhat similar methods to express the image position of an object in terms of the separations of the surfaces and the height of the intercepts of a standard ray on the different surfaces.

Mr. T. SMITH, in reply, agreed that if one had time to go into all the cases which might arise many interesting and useful results would follow. It was easy from the formulæ he had quoted to obtain an idea of what other general relations are likely to exist in an optical system, and to extend the meaning to be attributed to various conditions, such, for example, as the sine condition of Abbé. He hoped to treat more fully of these matters later.

A paper on "*The Accuracy of the Lens and Drop Method of Measuring Refractive Index*" by Mr. H. REDMAYNE NETTLETON, B.Sc., was taken as read in the absence of the author.

The paper describes a simple arrangement for comparing on an optical bench the refractive indices of liquids for monochromatic light by the lens and drop method. The accuracy and sensibility of the method are discussed, special stress being laid on the choice of lenses and on the manner of correcting for the thickness of lens used. Attention is drawn to the accuracy obtainable in measuring a small radius of curvature of a lens face in terms of the well known refractive index of water, and in measuring the refractive index of the glass of a lens.

## NOTICES OF BOOKS.

*Brazil.* By J. C. OAKENFULL. Frome: Butler and Tanner.

THIS handbook is full of valuable information about the history, resources, and industries of Brazil, and will be invaluable to intending settlers and visitors. Details of the laws and customs of the different parts of the country are included, and many maps, plans, and illustrations are given. In addition a really useful bibliography is provided, and the regulations regarding colonisation and immigration are reprinted.

*Extinction des Radiations Solaires dans l'Atmosphère Terrestre.* ("Extinction of Solar Radiations in the Terrestrial Atmosphere"). By F. LINDHOLM. Upsala: Librairie A.B. Akademiska Bokhandeln.

THE experiments described in this monograph had for their object the determination of the coefficient of atmospheric transmission, and were carried out at the Physical Institute of the University of Upsala. The spectrophotometric method was adopted, and the experimental arrangements and process of taking the measurements are explained in detail, with full tables of the results obtained. It was found that the transmission decreases with the wave-length, the values calculated for the extreme infra-red being uncertain and often forming exceptions to the general rule.

*L'Expédition Franco-Suédoise de Sondages Aériens à Kiruna.* ("The Franco-Swedish Expedition of Aerial Soundings at Kiruna"). By H. MAURICE. Upsala: Librairie A.B. Akademiska Bokhandeln.

THIS monograph contains interesting details of the Franco-Swedish expedition sent to Kiruna to study the temperature, &c., of the upper atmosphere. For this purpose 24 balloons containing registering instruments were sent up

in three series in the years 1907-8-9, 16 of them being found and returned by the finders some time (occasionally years) after having been liberated. The results were compared with those obtained by similar experiments made near Paris and in tropical regions. It was found that in the Polar circle, as in medium latitudes, there is a zone throughout which the temperature no longer decreases as the altitude increases, but may even become higher—the stratosphere. The temperature of the upper air (above 14,000 m.) in winter in the Polar circle is not lower than that above Paris at the same height, though the temperature of the earth is a good deal lower, and the average temperature is higher above Lapland than in Equatorial regions at the same altitude.

## CORRESPONDENCE.

 $\beta$ -NAPHTHOL IN DISINFECTANTS.

To the Editor of the Chemical News.

SIR,—On folio 286 of your last week's issue, in the report of the meeting of the Society of Public Analysts, there is an abstract of a paper by Mr. Bodmer on  $\beta$ -naphthol in disinfectants. In the report it states that Mr. Bodmer found that "*Richmond (Analyst, 1907, xxxii., 151)* recommends a diazotised benzidine solution for the detection of  $\beta$ -naphthol in milk." I would ask you to state that the paper in which the solution is described is by Mr. E. Holl Miller and myself. It was due to a suggestion of his that tetrazonium salts condensed easily with  $\beta$ -naphthol in neutral solution to form a fine red colouring matter while other phenolic compounds condensed with difficulty, that we worked out the method depending on the use of benzidine for the detection of  $\beta$ -naphthol, and I am anxious that Mr. Miller's name should have at least equal prominence with my own.—I am, &c.,

H. DROOP RICHMOND.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Bulletin de la Société Chimique de France.*  
Vol. xvii.-xviii., No. 6, 1915.

**Cuprous Carbonate.**—P. Carles.—When the amoniocal compound of copper is prepared by subjecting copper alternately to the action of air and liquid ammonia the process comes to a standstill after a time. This is due to the action of the carbon dioxide of the air which forms a protective layer of cupric carbonate. If this is left in contact with the metal cuprous carbonate is formed. It is a green powder, insoluble in pure water and in water containing ammonia, and fairly stable in air. It dissolves in acids with effervescence.

**Dehydration and Etherification of Cyclohexanol and *p*-Methylcyclohexanol by Oxalic Acid.**—M. A. Juéry.—When three molecules of oxalic acid are employed to dehydrate one of cyclohexanol good yields of hydrocarbon are obtained. If less than two molecules are used the proportion of hydrocarbon is reduced, and the oxalic ethers of the cyclohexanol are obtained. With one molecule of acid to two of alcohol etherification occurs but no dehydration. The author has prepared two neutral oxalic ethers of *p*-methylcyclohexanol, one crystallised and the other liquid, which are possibly the two isomers foretold theoretically.

**Transformation of Antipyrine into Diantipyrinemethane by Formic Aldehyde.**—Ch. Astré.—Antipyrine can be transformed into diantipyrinemethane in a few minutes by the action of formic aldehyde in presence of water only. A trace of alkali is sufficient to retard the action and render it incomplete. Pyramidon acts still more energetically than mineral alkalies, and absolutely stops the transformation.

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